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Selected Processes

IT Enviroscience
Knoxville, TN

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F. D. Hobbs C. W. Stuewe S. W. Dylewski
D. M. Pitts C. A. Peterson

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume presents in-depth studies of several major organic chemical products.

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Volume 7: Selected Processes

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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INTRODUCTION

A. SOCMI PROGRAM

Concern over widespread violation of the national ambient air quality standard for ozone (formerly photochemical oxidants) and over the presence of a number of toxic and potentially toxic chemicals in the atmosphere led the Environmental Protection Agency to initiate standards development programs for the control of volatile organic compound (VOC) emissions. The program goals were to reduce emissions through three mechanisms: (1) publication of Control Techniques Guidelines to be used by state and local air pollution control agencies in developing and revising regulations for existing sources; (2) promulgation of New Source Performance Standards according to Section 111(b) of the Clean Air Act; and (3) promulgation, as appropriate, of National Emission Standards for Hazardous Air Pollutants under Section 112 of the Clean Air Act. Most of the effort was to center on the development of New Source Performance Standards.

One program in particular focused on the synthetic organic chemical manufacturing industry (SOCMI), that is, the industry consisting of those facilities primarily producing basic and intermediate organics from petroleum feedstock meterials. The potentially broad program scope was reduced by concentrating on the production of the nearly 400 higher volume, higher volatility chemicals estimated to account for a great majority of overall industry emissions. EPA anticipated developing generic regulations, applicable across chemical and process lines, since it would be practically impossible to develop separate regulations for 400 chemicals within a reasonable time frame.

To handle the considerable task of gathering, assembling, and analyzing data to support standards for this diverse and complex industry, EPA solicited the technical assistance of IT Enviroscience, Inc., of Knoxville, Tennessee (EPA Contract No. 68-02-2577). IT Enviroscience was asked to investigate emissions and emission controls for a wide range of important organic chemicals. Their efforts focused on the four major chemical plant emission areas: process vents, storage tanks, fugitive sources, and secondary sources (i.e., liquid, solid, and aqueous waste treatment facilities that can emit VOC).

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B. REPORTS

To develop reasonable support for regulations, IT Enviroscience gathered data on about 150 major chemicals and studied in-depth the manufacture of about 40 chemical products and product families. These chemicals were chosen considering their total VOC emissions from production, the potential toxicity of emissions, and to encompass the significant unit processes and operations used by the industry. From the in-depth studies and related investigations, IT Enviroscience prepared 53 individual reports that were assembled into 10 volumes. These ten volumes are listed below:

Volume 1 : Study Summary
Volume 2 : Process Sources
Volume 3 : Storage, Fugitive, and Secondary Sources
Volume 4 : Combustion Control Devices
Volume 5 : Adsorption, Condensation, and Absorption Devices
Volume 6-10: Selected Processes

This volume is a compilation of individual reports for the following chemical products: nitrobenzene, aniline, cumene, toluene diisocyanate, terephthalic acid, dimethyl terephthalate, phenol, acetone, and linear alkylbenzene. The reports generally describe processes used to make the products, VOC emissions from the processes, available emission controls, and the costs and impacts of those controls (except that abbreviated reports do not contain control costs and impacts). Information is included on all four emission areas; however, the emphasis is on process vents. Storage tanks, fugitive sources, and secondary sources are covered in greater detail in Volume III. The focus of the reports is on control of new sources rather than on existing sources in keeping with the main program objective of developing new source performance standards for the industry. The reports do not outline regulations and are not intended for that purpose, but they do provide a data base for regulation development by EPA.

C. MODEL PLANTS

To facilitate emission control analyses, the reports introduce the concept of a "model plant" (not in abbreviated reports). A model plant by definition is a representation of a typical modern process for production of a particular chemical. Because of multiple production routes or wide ranges in typical production capacities, several model plants may be presented in one product report. The model plants can be used to predict emission characteristics of a new plant. Of course, describing exactly what a new plant will be like is difficult because variations of established production routes are often practiced by individual companies. Nonetheless, model plants provide bases for making new-plant emission estimates (uncontrolled and controlled), for selecting and sizing controls for new plants, and for estimating cost and environmental impacts. It is stressed that model-plant analyses are geared to new plants and therefore do not necessarily reflect existing plant situations.

REPORT 1

NITROBENZENE

F. D. Hobbs
C. W. Stuewe

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

February 1981

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Nitrobenzene was selected for consideration because preliminary estimates indicated that its production caused relatively high emissions of volatile organic compounds (VOC).[1] The main constituent of these emissions is benzene, which was included as a hazardous pollutant by the EPA in the Federal Register on June 8, 1977. Also, the growth rate of nitrobenzene production is expected to be higher than the average growth rate for the industry.

Nitrobenzene is a relatively nonvolatile liquid under ambient conditions (see Appendix A for pertinent physical properties). Most emissions from its production are due to the volatility of benzene, the primary feed material.

B. USAGE AND GROWTH

Approximately 97% of all nitrobenzene produced is consumed in the manufacture of aniline. Therefore the consumption pattern for aniline is the dominant factor in the usage of nitrobenzene and its production growth. Table II-1 lists the end uses of aniline, with the percentage of production used for each end use, and the expected growth rates. The use of nitrobenzene as a solvent accounts for most of the remaining consumption.

Nitrobenzene production in 1978 was reported[2] to have been 261,000 Mg, which is 51% of the capacity on-line at that time.[3] Nitrobenzene production would utilize 60% of the estimated 1982 capacity,[3,4] with an average annual growth of 7% assumed.

Five producers were operating seven nitrobenzene plants at the first of 1979. Table II-2 lists the producers and their capacities, and Fig. II-1 shows their locations. All these plants produce nitrobenzene by nitrating benzene with nitric acid mixed with sulfuric acid.[3] Several recent developments have affected the status of nitrobenzene capacity: Cyanamid reactivated its Bound Brook, NJ, plant in 1978 and announced plans to bring a new nitrobenzene facility of unspecified capacity on-stream in 1979; Dupont expanded the capacities at their Beaumont, TX, and Gibbstown, NJ, facilities by a total of about

Table II-1. Aniline Usage and Growth[a]

End Use	Percentage of Production (1978)	Average Rate Growth (%/yr)
Polymeric isocyanates	52	8
Rubber chemicals	29	2—3
Dyes and intermediates	4	3
Hydroquinone	3	4.5
Drugs, pesticides, and miscellaneous	12	6

[a] See ref 3.

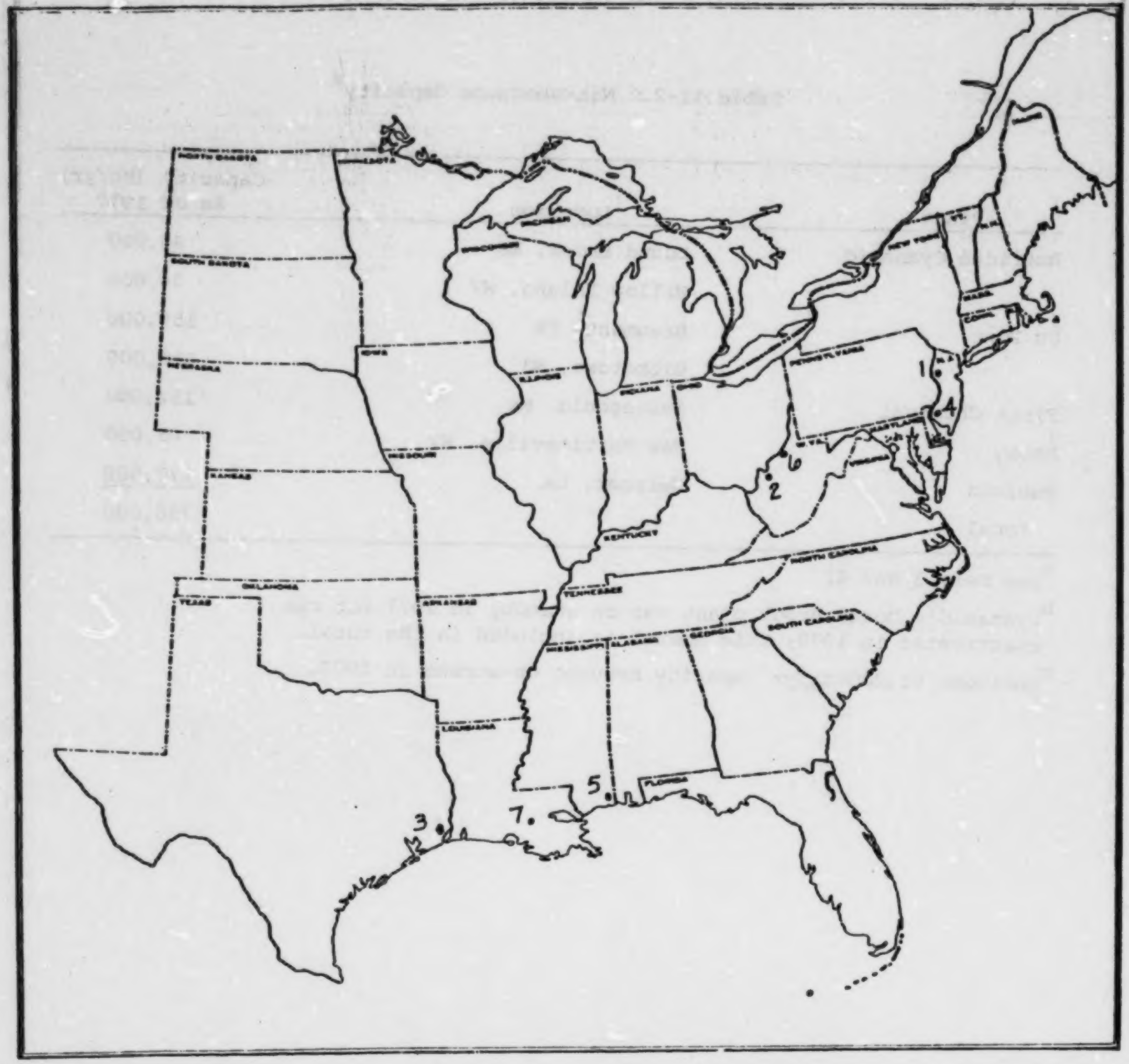
Table II-2. Nitrobenzene Capacity[a]

Plant	Location	Capacity (Mg/yr) As of 1977
American Cyanamid	Bound Brook, NJ	48,000
	Willow Island, WV	34,000
Du Pont	Beaumont, TX	159,000
	Gibbstown, NJ	110,000
First Chemical	Pascagoula, MS	152,000
Mobay	New Martinsville, WV	85,000
Rubicon	Geismar, LA	170,000
Total		758,000

[a] See refs 3 and 4.

[b] Cyanamid's Bound Brook plant was on standby in 1977 but was reactivated in 1978; this amount is included in the total.

[c] Includes 61,200-Mg/yr capacity brought on-stream in 1977.



1. American Cyanamid, Bound Brook, NJ
2. American Cyanamid, Willow Island, WV
3. Du Pont, Beaumont, TX
4. Du Pont, Gibbstown, NJ
5. First Chemical, Pascagoula, MS
6. Mobay, New Martinsville, WV
7. Rubicon, Geismar, LA

Fig. II-1. Nitrobenzene Manufacturing Locations

40,000 mg/yr (about 20,000 mg/yr at each plant) in 1978; First Chemical expanded capacity by about 92,000 Mg in 1977; Mobay is to increase capacity by 25,000 Mg by 1980; and Rubicon increased capacity by about 136,000 Mg during 1978. Allied at Moundsville, WV, and Monsanto at Sauget, IL, discontinued nitrobenzene production during the mid-1970s.[3]

C. REFERENCES*

1. T. C. Gunn and K. L. Ring, "Benzene," p. 618.5023V in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1977).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION

Nitrobenzene is produced commercially by the direct nitration of benzene with a mixture of nitric acid, sulfuric acid, and water.[1,2] About 97% of the nitrobenzene is used captively to produce aniline.[3] There are no known foreign processes significantly different from the one used in the United States.

B. NITRATION OF BENZENE

Nitrobenzene is produced by the highly exothermic reaction

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(nitric acid)}}{HNO_3} \xrightarrow{H_2SO_4} \underset{\text{(nitrobenzene)}}{C_6H_5NO_2} + \underset{\text{(water)}}{H_2O}$$

The heat released from this reaction is about 1.8 MJ/kg.[4] The quantity of organic by-products formed, primarily nitrated phenols, is only about 0.02 wt % of the nitrobenzene produced.[5] Typically, these phenolic materials are discharged with the wastewater effluent.

A typical continuous-process flow diagram for the basic process is shown in Fig. III-1.

Benzene is nitrated at 55°C under atmospheric pressure by a mixture of concentrated nitric (Stream 1) and sulfuric (Stream 2) acids in a series of continuous stirred-tank reactors. The exothermic heats of nitration and dilution are removed by cooling coils. Yields of 96 to 98% of theory[2] are reported.

The crude reaction mixture (Stream 3) flows to the separator, where the organic phase is decanted from the aqueous waste acid.

The acid phase (Stream 4) is contacted in the extractor with fresh benzene from storage (Stream 5)[6--8] to extract most of the dissolved nitrobenzene and nitric acid before the stream is stored in the waste-acid tank.

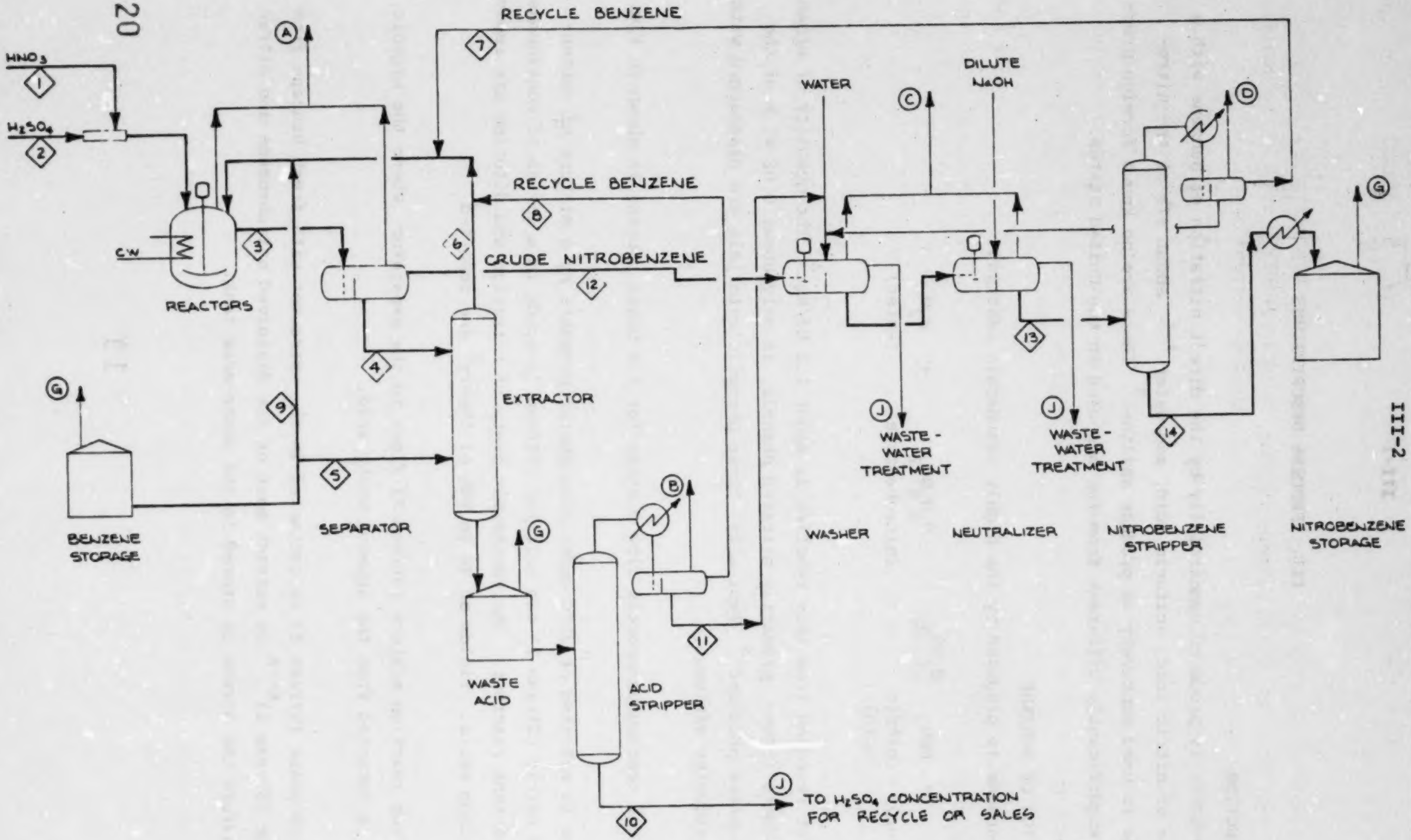
RECYCLE BENZENE
A
7
HNO3
1
H2SO4
2
C.W
3
REACTORS
RECYCLE BENZENE
8
6
CRUDE NITROBENZENE
12
4
9
5
G
BENZENE STORAGE
SEPARATOR
EXTRACTOR
G
WASTE ACID
B
11
ACID STRIPPER
10
J
TO H2SO4 CONCENTRATION FOR RECYCLE OR SALES
WATER
C
DILUTE NaOH
D
G
13
J
WASTE - WATER TREATMENT
J
WASTE - WATER TREATMENT
14
WASHER
NEUTRALIZER
NITROBENZENE STRIPPER
NITROBENZENE STORAGE

Fig. III-1. Process Flow Diagram for Manufacture of Nitrobenzene

Benzene extract (Stream 6), two recovered and recycled benzene streams (7 and 8), and as much additional benzene (Stream 9) as is required make up the benzene charge to the reaction step.

It is common practice to recover the benzene from the waste acid by distillation in the acid stripper for recycle (Stream 8) to the reactor. The stripped acid (Stream 10) is usually reconcentrated on-site but may be sold.[9] Water carried overhead with the benzene is forwarded (Stream 11) to the washer.

Crude nitrobenzene from the separator (Stream 12) is washed first with water and then dilute caustic soda to remove the mineral acids and organic acids, such as the nitrophenols.[5] The washer and neutralizer effluents are discharged to wastewater treatment.[6,7,9] Following neutralization, the organic layer (Stream 13) is fed to the nitrobenzene stripper, where water and most of the benzene and other low boilers are carried overhead.[6--9] The organic phase, primarily benzene, is decanted and recycled (Stream 7) to the reactor, and the aqueous phase is sent to the washer.[6,7] Stripped nitrobenzene (Stream 14) is cooled and then transferred to nitrobenzene storage for subsequent use as feed to an on-site aniline process.

Typically, many of the process steps are padded with nitrogen gas to reduce the chances of fire or explosion.[6--8,10] This nitrogen padding gas and other inert gases are purged from vents associated with the reaction and separator (Vent A), the condenser on the acid stripper (Vent B), the washer and neutralizer (Vent C), and the condenser on the nitrobenzene stripper (Vent D).

Fugitive emissions of benzene and nitrobenzene can occur when leaks develop in valves, pump seals, and other equipment. Leaks can also occur from corrosion by the sulfuric and nitric acids and hinder control of fugitive emissions.

All transfers of the product are by pipeline and there are no handling emissions.

Storage emissions (G on Fig.III-1) occur from tanks storing benzene, waste acid, and nitrobenzene.

Three potential sources of secondary emissions (J on Fig.III-1) are the aqueous waste from the washer, the caustic effluent from the neutralizer, and the waste acid from the acid stripper.

C. PROCESS VARIATIONS

Another practiced process variation is to not strip residual benzene out of the waste acid before sale or reconcentration of this acid. This can significantly affect emissions unless the acid reconcentration process is adequately controlled.

D. REFERENCES*

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. NITROBENZENE MODEL PLANTS

Three model plant capacities -- 30,000, 90,000, and 150,000 Mg/yr -- were selected to represent current domestic nitrobenzene manufacturing facilities. The model process* (Fig. III-1) best represents today's nitrobenzene manufacturing and engineering technology.

Typical raw material, waste acid, and product storage capacities were selected for the three model-plant capacities. The number of valves and pumps selected was based on data from an existing facility.[1] Characteristics of the model plants important to air dispersion are given in Appendix B.

B. SOURCES AND EMISSIONS

1. General

Sources and emission rates for the model plants are summarized in Table IV-1. Process and secondary emissions are based on data obtained from plant-site visits and information submitted to the EPA.[1--4] Storage emissions were calculated with the equations in AP-42.[5] However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[6] Fugitive emissions were determined by

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*See p. I-2 for a discussion of model plants.

Table IV-1. Uncontrolled Benzene and Total VOC from Nitrobenzene Model Plants

Source	Stream Designation (Fig. III-1)	Emission Rates											
		For 30,000-Mg/yr Model Plant				For 90,000-Mg/yr Model Plant				For 150,000-Mg/yr Model Plant			
		Ratio[b] (kg/Mg)		Rate (kg/hr)		Ratio[b] (kg/Mg)		Rate (kg/hr)		Ratio[b] (kg/Mg)		Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC
Reactor and separator	A	0.960	0.965	3.29	3.30	0.960	0.965	9.86	9.91	0.960	0.965	16.4	16.5
Waste-acid stripper	B	0.170	0.170	0.582	0.582	0.170	0.170	1.75	1.75	0.170	0.170	2.91	2.91
Wash and neutralization	C	0.0081	0.0107	0.0277	0.0366	0.0081	0.0107	0.0832	0.110	0.0081	0.0107	0.139	0.183
Nitrobenzene stripper	D	0.170	0.171	0.582	0.586	0.170	0.171	1.75	1.76	0.170	0.171	2.91	2.93
Small benzene storage[c]	G	0.076	0.076	0.262	0.262	0.078	0.078	0.797	0.797	0.077	0.077	1.31	1.31
Waste-acid storage	G	0.052	0.052	0.177	0.177	0.051	0.051	0.526	0.526	0.048	0.048	0.830	0.830
Benzene storage	G	0.294	0.294	1.01	1.01	0.283	0.283	2.91	2.91	0.281	0.281	4.81	4.81
Nitrobenzene storage	G		0.0024		0.0083		0.0019		0.0197		0.0018		0.031
Fugitive	H	1.9	2.98	6.5	10.2	0.63	0.99	6.5	10.2	0.38	0.596	6.5	10.2
Secondary	J	0.10	0.33	0.342	1.10	0.10	0.33	1.03	3.39	0.10	0.33	1.71	5.65
Total		3.73	5.05	12.8	17.3	2.45	3.05	25.2	31.4	2.19	2.65	37.5	45.4

[a] Uncontrolled emissions are emissions from the process employing no additional control devices other than that necessary for economical operation.

[b] kg of benzene or total VOC per Mg of nitrobenzene produced.

[c] The small storage tank contains approximately one day's supply of benzene; the large tank is referred to as the main storage tank.

estimating the number of valves and pumps for the model plants based on information from an existing facility[1] and applying the factors listed in Appendix C. Handling losses are not considered, since it is assumed that the nitrobenzene will be used on-site for production of aniline.

2. Process Emissions

There are four vents for process emissions from the model plants, two of which are combined vents from associated equipment. All these vents are necessary for removal of inert gases from the process. Nitrogen padding of benzene is used for safety purposes and contributes to inert gases in the process and resultant emissions. Benzene constitutes the bulk of emissions from the process, as shown in Table IV-1, with less nitrobenzene being emitted because of its low volatility.

a. Reactor and Separator Vent -- This vent (Vent A, Fig. III-1) combines emissions from the reactors and from the separator. Oxides of nitrogen are generated by side reactions involving nitric acid and must be purged from the process, along with nitrogen padding gas.

b. Acid Stripper Vent -- Organics are stripped from the waste acid for recycle to the process, and noncondensables are vented (Vent B, Fig. III-1) from the associated condenser.

c. Washer and Neutralizer Vent -- The washer removes mineral acids from the nitrobenzene, and the neutralizer removes the remaining acids, primarily organic acids. The combined vent (Vent C, Fig. III-1) for these two operations removes nitrogen padding gas and some water vapor from the process.

d. Nitrobenzene Stripper Vent -- Benzene is stripped from the nitrobenzene, and noncondensables, primarily nitrogen padding gas, are vented (Vent D, Fig. III-1) from the associated condenser.

3. Storage Emissions

Emissions result from the storage of benzene, waste acid (which contains benzene), and nitrobenzene. The sources of storage emissions for the model plants are shown on the flow diagram, Fig. III-1 (Source G). Storage tank conditions for the model plants are given in Table IV-2. The uncontrolled storage emissions in Table IV-1 were calculated with the equations from AP-42[5] with the breathing loss adjustment[6] as mentioned above and the assumption that fixed-roof tanks are used; on the average these tanks are half full and have a 12°C diurnal temperature variation. It was also assumed that the waste-acid and nitrobenzene storage tanks are operated at nearly constant levels, with only six turnovers per year, and that waste-acid stripping does not remove all the benzene from that material before storage.

4. Fugitive Emissions

Process pumps and valves are potential sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves based on data from an existing facility.[1] All pumps have mechanical seals. Twenty-five percent of these pumps and valves are being used in benzene service. The fugitive emissions included in Table IV-1 are based on the factors given in Appendix C.

5. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of process waste liquid. For the model plants three potential sources of secondary emissions from waste liquids are indicated on the flow diagram, Fig. III-1 (Source J). These sources are the sulfuric acid from the acid stripper, wastewater from the nitrobenzene washer, and waste caustic from the nitrobenzene neutralizer. Because of its low volatility most of the nitrobenzene in the waste acid will make no contribution to secondary emissions except when the acid is being concentrated for reuse. Any benzene remaining after the acid is stripped would create a potential for secondary emissions. Emissions from this source will be discussed more fully in a future EPA report on concentration of sulfuric acid used in organic chemical processing. The combined wastewater from the wash and neutralization steps contains benzene, nitrobenzene, and neutralized organic acid by-products (primarily nitrophenates). The latter are nonvolatile and will not contribute to the VOC emission rate. Secondary emissions of nitrobenzene from the wastewater directed to a clarifier and conventional air-activated sludge treatment system will be low due to the low vapor pressure at ambient temperatures and the biodegradability of the nitrobenzene. The loss, estimated by methods to be described in a future EPA report on secondary emis-

Table IV-2. Storage Parameters for Determining Model-Plant Emissions

Content	Tank Size (m^3)	Turnovers per Year	Bulk Liquid Temperature (°C)
For 30,000-Mg/yr Model Plant			
Benzene	946	24	20
Benzene	95	236	20
Waste acid[a]	151	6	45
Nitrobenzene[a]	473	6	40
For 90,000-Mg/yr Model Plant			
Benzene	2840	24	20
Benzene	284	236	20
Waste acid[a]	454	6	45
Nitrobenzene[a]	1420	6	40
For 150,000-Mg/yr Model Plant			
Benzene	4730	24	20
Benzene	473	236	20
Waste acid[a]	757	6	45
Nitrobenzene[a]	2360	6	40

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[a] Surge tanks normally operated at constant level.

sions, is 1.1% of the nitrobenzene in the untreated water. This is equivalent to an emission rate of 5 X 10^{-3} kg of VOC per Mg of nitrobenzene produced. The benzene and total VOC secondary emissions listed in Table IV-1 were calculated on the assumption that the benzene and 1.1% of the nitrobenzene in the wastewater effluent will become secondary emissions.

C. EFFECTS OF PROCESS VARIATIONS ON EMISSIONS

Waste acid, which is not stripped of residual benzene before being sold or reconcentrated, can significantly affect secondary emissions. Based on solubility data the potential emissions from this source could be as much as 1 kg of benzene per Mg of nitrobenzene produced.

Most plants use nitrogen blanketing on many of the process steps. The effects on emissions from not using nitrogen blanketing have not been defined.

D. REFERENCES*

1. C. W. Stuewe, IT Enviroscience, Trip Report for Visit to E. I. du Pont de Nemours & Co., Beaumont, TX, Sept. 7,8, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

2. R. Barker, First Chemical Corporation, letter to D. R. Goodwin, EPA, Jan. 20, 1978.

3. D. W. Smith, E. I. du Pont de Nemours & Co., letter to D. R. Goodwin, EPA, Feb. 3, 1978.

4. L. P. Hughes, Mobay Chemical Corporation, letter to D. R. Goodwin, EPA, Jan. 31, 1978.

5. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-1 to 4.3-11 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

6. E. C. Pulaski, TRW, letter dated May 30, 1979, to Richard Burr, EPA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. PROCESS SOURCES

A number of control systems are feasible and were considered for control of the combined process emissions. In-process storage emissions can be readily controlled in conjunction with the process emissions and were so treated.

1. Vent Absorber

An absorber using nitrobenzene as the scrubbing solvent has been selected for detailed study. Absorption of a volatile hydrocarbon in a less volatile hydrocarbon is a common method for recovery of light hydrocarbons and can be used for absorption of benzene in nitrobenzene. The use or intended use of this type of control device has been reported by two producers.[1,2]

The absorber system described on page D-5 in Appendix D is a preliminary design for cost estimating purposes per the standard design methods described by Treybal.[3] The design has not been optimized. The absorbent and absorbed materials are used or produced in the process and therefore very little additional processing equipment is required for recovery of most of the emitted VOC. As designed the system utilizes the existing process capability for separation of benzene and nitrobenzene by recycling the liquid bottoms stream from the absorber to the nitrobenzene stripper. It is assumed that the existing nitrobenzene stripper capacity is sufficient to handle this additional load. Estimated capital equipment costs would be increased if additional stripping capacity is required. Nitrobenzene absorbent is drawn from storage and chilled to 15°C before it enters the absorbing column. Exhaust gases from the nitrobenzene scrubbing section pass through additional scrubbing sections, where they are washed with water and dilute caustic solution to remove oxides of nitrogen.[4] The vent absorption system will reduce benzene and total VOC emissions by about 95% at a pressure of 1×10^5 Pa.

Controlled emissions, based on this control device, are given in Table V-1 for the 30,000-, 90,000-, and 150,000-Mg/yr model plants.

Table V-1. Controlled Benzene and Total VOC Emissions for Nitrobenzene Model Plants

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emission Data Ratio[a] (kg/Mg)		Emission Data Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
For 30,000-Mg/yr Model Plant							
Reactor and separator	A						
Waste-acid stripper	B	Vent absorber	94.6	0.0775	0.0780	0.237	0.267
Wash and neutralization	C	Thermal oxidizer	99.0	0.0144	0.0144	0.0440	0.0494
Nitrobenzene stripper	D						
Small benzene storage	G						
Waste-acid storage	G						
Benzene storage	G	Floating roof	88	0.0441	0.0441	0.151	0.151
Nitrobenzene storage	G	None			0.0024		0.0083
Fugitive	H	Detect and correct leaks plus mechanical seals	67.7	0.50	1.08	1.70	3.7
Secondary	J	None		0.10	0.33	0.342	1.10
Total with vent absorber				0.72	1.53	2.43	5.23
Total with thermal oxidizer				0.66	1.47	2.24	5.01
For 90,000-Mg/yr Model Plant							
Reactor and separator	A						
Waste-acid stripper	B						
Wash and neutralization	C	Vent absorber	94.6	0.0776	0.0781	0.797	0.802
Nitrobenzene stripper	D	Thermal oxidizer	99.0	0.0144	0.0145	0.148	0.149
Small benzene storage	G						
Waste-acid storage	G						
Benzene storage	G	Floating roof	85	0.0425	0.0425	0.437	0.437
Nitrobenzene storage	G	None			0.0019		0.0197
Fugitive	H	Detect and correct leaks plus mechanical seals	67.7	0.165	0.36	1.7	3.7
Secondary	J	None		0.10	0.33	1.03	3.39
Total with vent absorber				0.39	0.81	3.96	8.32
Total with thermal oxidizer				0.22	0.75	3.32	7.70
For 150,000-Mg/yr Model Plant							
Reactor and separator	A						
Waste-acid stripper	B						
Wash and neutralization	C	Vent absorber	94.6	0.0774	0.0779	1.32	1.33
Nitrobenzene stripper	D	Thermal oxidizer	99.0	0.0143	0.0144	0.245	0.247
Small benzene storage	G						
Waste-acid storage	G						
Benzene storage	G	Floating roof	85	0.0421	0.0421	0.721	0.721
Nitrobenzene storage	G	None			0.0018		0.031
Fugitive	H	Detect and correct leaks plus mechanical seals	67.7	0.099	0.216	1.70	3.7
Secondary	J	None		0.10	0.33	1.71	5.65
Total with vent absorber				0.32	0.67	5.45	11.43
Total with thermal oxidizer				0.26	0.60	4.38	10.35

[a] kg of benzene or total VOC per Mg of nitrobenzene produced.

2. Thermal Oxidizer

Efficient control of benzene and total VOC is technically feasible with the use of thermal oxidation. It is estimated that, with effective design, the removal efficiency for VOC can be greater than 99%.

The details of the system necessary for cost estimation for the 90,000-Mg/yr model plant are described in Appendix D. Two combustion chambers are included to reduce NO_x emissions by reducing the NO_x to N_2. Heat recovery on such a small unit is not economical and was not included.

Controlled emissions, based on this control device, are given in Table V-1 for the 30,000-, 90,000-, and 150,000-Mg/yr model plants.

With adequate design consideration, efficient VOC removal can be accomplished by thermal oxidation of the vent stream in an existing boiler, in a process equipment heater, or in a liquid thermal oxidizer. Technical feasibility and economics for such an approach would be highly dependent on the specifics of each situation.

3. Chemical Absorber.

A system that consists of an absorption column that removes benzene by nitration in a circulating mixture of nitric and sulfuric acids has been reported in use with a design efficiency of greater than 99.9% for benzene removal.[1] Subsequently it was reported that operating difficulties had been experienced with the column and that it has been converted to a scrubber using nitrobenzene. A chemical (nitration) absorber system similar to that reported is described on page D-19 in Appendix D. The reaction products and remaining acids are returned to the primary nitration step in the process. Exhaust gases pass into a scrubber, where they are washed with water and dilute caustic solution to remove acids and oxides of nitrogen.[4] Conceptually, an absorbing reactor, for this application should be technically feasible with relatively attractive economics; however, the technical practicality has not been proved by actual operation.

B. FUGITIVE SOURCES

Control for fugitive sources will be discussed in a future document covering fugitive emissions from the synthetic organic chemicals manufacturing industry

(SOCMI). The controlled fugitive emissions given in Table V-1 were calculated with the factors listed in Appendix C. These factors are based on the assumption that any major leaks will be detected and repaired.

C. STORAGE SOURCES

Storage guidelines for SOCMI are given in a separate EPA document.[5] Emissions from the benzene daily-storage tank* and waste-acid storage tank are controlled in conjunction with the process emissions that are controlled by the absorbing reactor. The main benzene feed storage emissions are controlled by using floating-roof tanks.** Storage emissions were calculated by asuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%.[6] Emissions from storage of nitrobenzene remain uncontrolled.

D. SECONDARY SOURCES

Potential secondary emissions originate with the waste acid, the wastewater from the nitrobenzene washer, and the waste caustic from the nitrobenzene neutralizer. Benzene discharged with the wastewater effluent will create a secondary emission because of its relatively high volatility. Because of its low volatility most of the nitrobenzene in the wastewater effluent will make no contribution to secondary emissions. The total estimated potential secondary emissions from the model plants are listed in Table V-1. Secondary emissions are uncontrolled. A separate EPA report discusses emissions from secondary sources.[7]

E. CONTROL DEVICES USED BY INDUSTRY

Control devices used by industry are covered in Appendix E.

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*Small storage tank contains approximately one day's supply of benzene; the larger tank is the main benzene storage tank.

**Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2nd ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

F. REFERENCES*

1. R. Barker, First Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 20, 1978.

2. W. C. Anthon, Rubicon Chemicals, letter to David A. Beck, EPA, Apr. 14, 1978.

3. R. E. Treybal, Mass-Transfer Operations, Chaps. 6 and 8, McGraw-Hill, New York, 1955.

4. E. F. Spencer, Jr., "Pollution Control in the Chemical Industry," Chap 14, p. 14-6 in Industrial Pollution Control Handbook edited by H. F. Lund, McGraw-Hill, New York, 1971.

5. D. G. Erikson, IT Enviroscience, Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, ND).

6. William T. Moody, TRW, letter dated Aug. 15, 1979, to D. Beck, EPA.

7. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

Table VI-1 shows the effect on the environment of reducing benzene and total VOC emissions by application of the described control systems to the model plants. Individual effects are discussed below.

1. Control of Process Emissions and Emissions from In-Process Storage of Benzene and Waste Acid

Process emissions and emissions from in-process storage of benzene and waste acid can be controlled by using either a vent absorber or a thermal oxidizer.

a. Vent Absorber -- A vent absorber using nitrobenzene as the absorbent can be installed for control of process emissions and emissions from in-process storage of benzene and waste acid. This vent absorber reduces benzene and total VOC by 40.8 and 41.0 Mg/yr for the 30,000-Mg/yr model plant, 122.4 and 123.1 Mg/yr for the 90,000-Mg/yr model plant, and 203.0 and 204.4 Mg/yr for the 150,000-Mg/yr model plant. The electrical energy required for operation of the vent absorber is small (less than 400 MJ/Mg of VOC recovered for the 90,000-Mg/yr model plant).

b. Thermal Oxidizer -- As an alternative device, a thermal oxidizer can be installed for control of process emissions and emissions from in-process storage of benzene and waste acid. This thermal oxidizer reduces benzene and total VOC by 42.7 and 42.9 Mg/yr for the 30,000-Mg/yr model plant, 128.1 and 128.8 Mg/yr for the 90,000-Mg/yr model plant, and 212.5 and 213.9 Mg/yr for the 150,000-Mg/yr model plant. The electrical energy required for operation of the thermal oxidizer is small (less than 100 MJ per Mg of VOC reduced).

2. Benzene Storage

Retrofitting existing fixed-roof tanks with floating roofs or installing new floating-roof tanks for control of emissions from the main benzene storage tanks reduces benzene emissions by 11.4, 30.8, and 50.4 Mg/yr for the 30,000-, 90,000-, and 150,000-Mg/yr model plants, respectively. The use of floating-roof storage tanks for emissions control does not consume energy and has no adverse environmental or energy impact.

Table VI-1. Environmental Impact of Controlled Model Plants

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (Mg/yr)[a] 30,000-Mg/yr Model Plant Benzene	30,000-Mg/yr Model Plant Total VOC	90,000-Mg/yr Model Plant Benzene	90,000-Mg/yr Model Plant Total VOC	150,000-Mg/yr Model Plant Benzene	150,000-Mg/yr Model Plant Total VOC
Reactor and separator[b]	A							
Waste-acid stripper[b]	B							
Wash and neutralization[b]	C	Vent absorber	40.8 (95%)[c]	41.0 (95%)	122.4 (95%)	123.1 (95%)	203.0 (95%)	204.4 (95%)
Nitrobenzene stripper[b]	D	Thermal oxidizer	42.7 (99%)	43.9 (99%)	128.1 (99%)	128.8 (99%)	212.5 (99%)	213.9 (99%)
Small benzene storage[b]	G							
Waste-acid storage[b]	G							
Benzene storage	G	Internal floating roof	11.4 (85%)	11.4 (85%)	30.8 (85%)	30.8 (85%)	50.4 (85%)	50.4 (85%)
Nitrobenzene storage	G	None						
Fugitive	H	Detect and correct minor leaks plus mechanical seals	42.0 (13.8%)	56.9 (613.7%)	42.0 (73.8%)	56.9 (63.7%)	42.0 (73.8%)	56.9 (63.7%)
Secondary	J	None						
Total with vent absorber			94.2	109.3	195.2	210.8	295.4	311.7
Total with thermal oxidizer			96.1	112.2	200.9	216.5	304.9	321.2

[a] Annual reduction is based on 8760 hr of operation.

[b] Combined for control.

[c] Figures in parentheses are the percent reduction of benzene and total VOC emissions.

3. Fugitive Emissions

Control of fugitive emissions is accomplished by detection and repair of major leaks plus mechanical seals on pumps. This reduces benzene emissions by 42.0 Mg/yr and total VOC emissions by 56.9 Mg/yr for each of the model plants. If each of the seven domestic production facilities operating in 1979 had an average number of pumps and valves equivalent to those in the model plants, the control of fugitive emissions for the industry would reduce the total industry benzene emissions by 294 Mg/yr and the total VOC emissions by 398 Mg/yr.

B. CONTROL COST IMPACT

This section presents estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of nitrobenzene. Details of the model plants are given in Sect. III, emission sources and emissions are discussed in Sect. IV, and cost estimate calculations are given in Appendix D.

Capital cost estimates represent the total investment required for purchase and installation of all new equipment for a complete emission control system, performing as defined for a typical location. These estimates do not include the cost resulting from production lost during installation of control systems or the costs for research and development.

The bases for annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors that were used are itemized in Table VI-2. Emission recovery credits are based on the current equivalent raw material market value of the material being recovered. Annual costs are for a 1-year period beginning in December 1979.

1. Process Emissions

Process emissions, emissions from daily-use storage of benzene, and emissions from waste acid storage are controlled by a vent absorber or a thermal oxidizer, which are shown in Appendix D. The estimated capital cost of installing the vent absorber is $41,500, $48,000, and $56,500 for the 30,000-, 90,000-, and 150,000-Mg/yr model plants, respectively. Utilities, related capital costs, and recovery credits vary with the plant capacity, as shown in Table VI-3. Installed capital and net annual cost variations with capacity are shown in

Table VI-2. Cost Factors Used in Computing Annual Costs

Item	Factor
Electricity	$0.00833/MJ ($0.03/kWh)
Operating time	8760 hr/yr
Operating labor	$15/hr
Fixed costs	
Maintenance labor plus materials, 6¢	29% installed capital
Capital recovery, 18% (10 yr life @ 12% int.)	
Taxes, insurance, administration charges, 5%	
Liquid-waste disposal	Minor; not considered
Recovery credits	
Benzene	$220/Mg ($0.10/lb)
Nitrobenzene (raw material value)	$220/Mg ($0.10/lb)

Figs. VI-1 and VI-2. The estimated capital cost of the installed thermal oxidizer, $277,000, does not vary for the three model plants because the unit is very small.

2. Storage

Model plant emissions from the small benzene storage tank and the waste-acid storage tank are controlled in conjunction with process emissions by the chemical absorber. Benzene-feed storage emissions are controlled by the use of floating-roof tanks. Another EPA report covers storage emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[1]

3. Fugitive Sources

Controlled emission factors for fugitive sources are described in Appendix C. A separate EPA document covers fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[2]

4. Secondary Sources

No control system has been defined for secondary emissions from the model plants. A separate EPA document discusses secondary sources and their control.[3]

Table VI-3. Emission Control Analyses for Nitrobenzene Model Plants

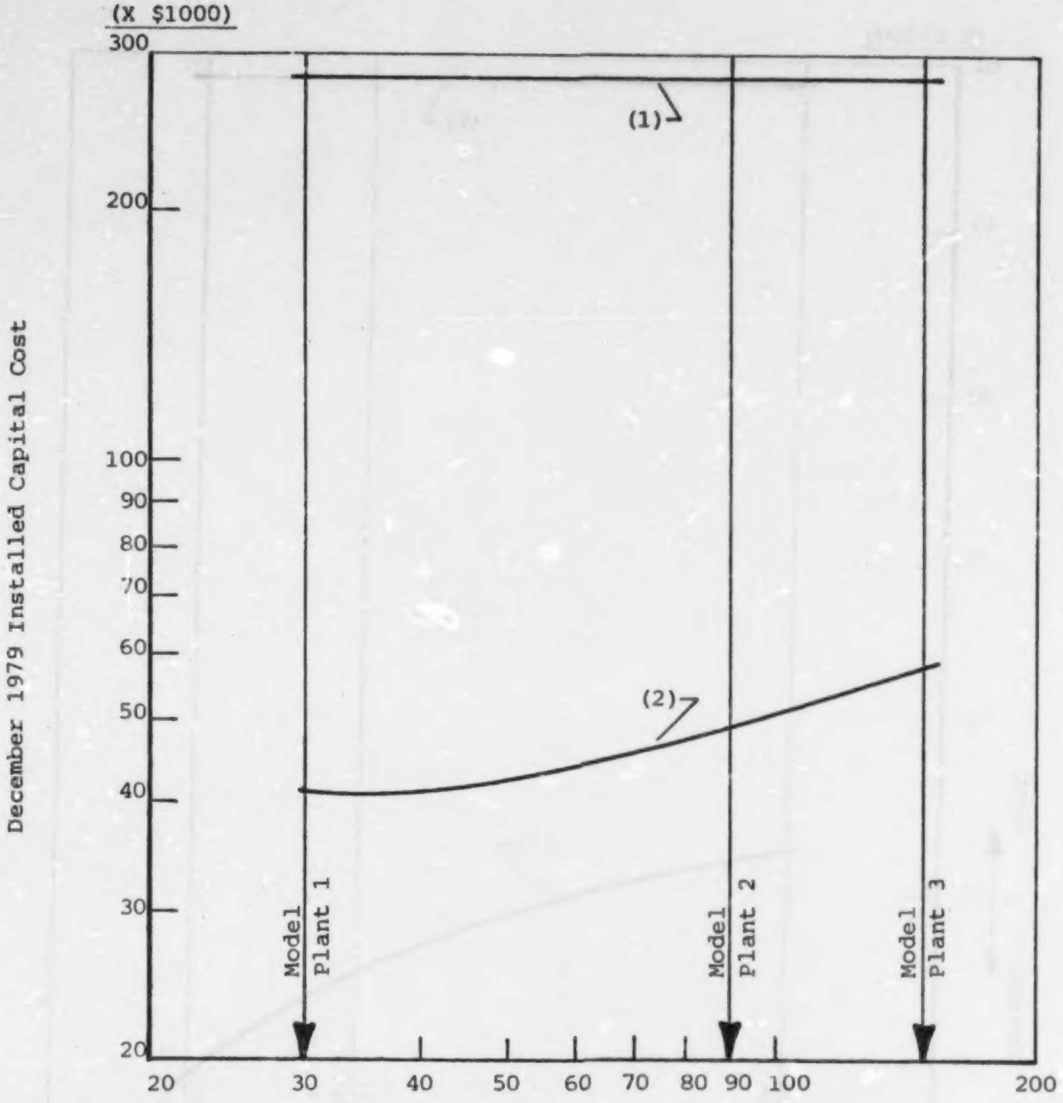
		Annual Operating Costs (X 1000) Mid-1978					(B) Emission Reduction			(C)[a]
Item	Total Installed Capital Cost (X 1000)	Utilities	Manpower	Capital Related Cost	Recovery Credits	(A) Net Annual Cost	Benzene (Mg/yr)	Total VOC[b] (Mg/yr)	Percent (for both)	Cost Effectiveness for Total VOC[b] (per Mg)
				30,000-Mg/yr Model Plant						
Vent absorber[c]	$ 41.5	$2.1		$12.0	$ 9.5	$ 4.6	40.8	41.0	95	$ 112
Thermal oxidizer[c]	277		$18.0	80.0		98.0	42.7	43.9	99	2,232
				90,000-Mg/yr Model Plant						
Vent absorber[c]	$ 48	$5.7		$13.9	$28.6	$(9.0)[d]	122.4	123.1	95	$ (73)[d]
Thermal oxidizer[c]	277		$18.0	80.0		98.0	128.1	128.8	99	760
				150,000-Mg/yr Model Plant						
Vent absorber[c]	$ 56.5	$9.5		$16.4	$47.7	$(21.8)[d]	203.0	204.4	95	$ (107)[d]
Thermal oxidizer[c]	277		$18.0	80.0		98.0	212.5	213.9	99	$ 458

[a] (C) = (A) ÷ (B).

[b] Total VOC consists of more than 99% benzene for the vent absorbers and thermal oxidizers.

[c] Controls process emissions and emissions from daily stored benzene and waste-acid storage.

[d] Net annual savings.

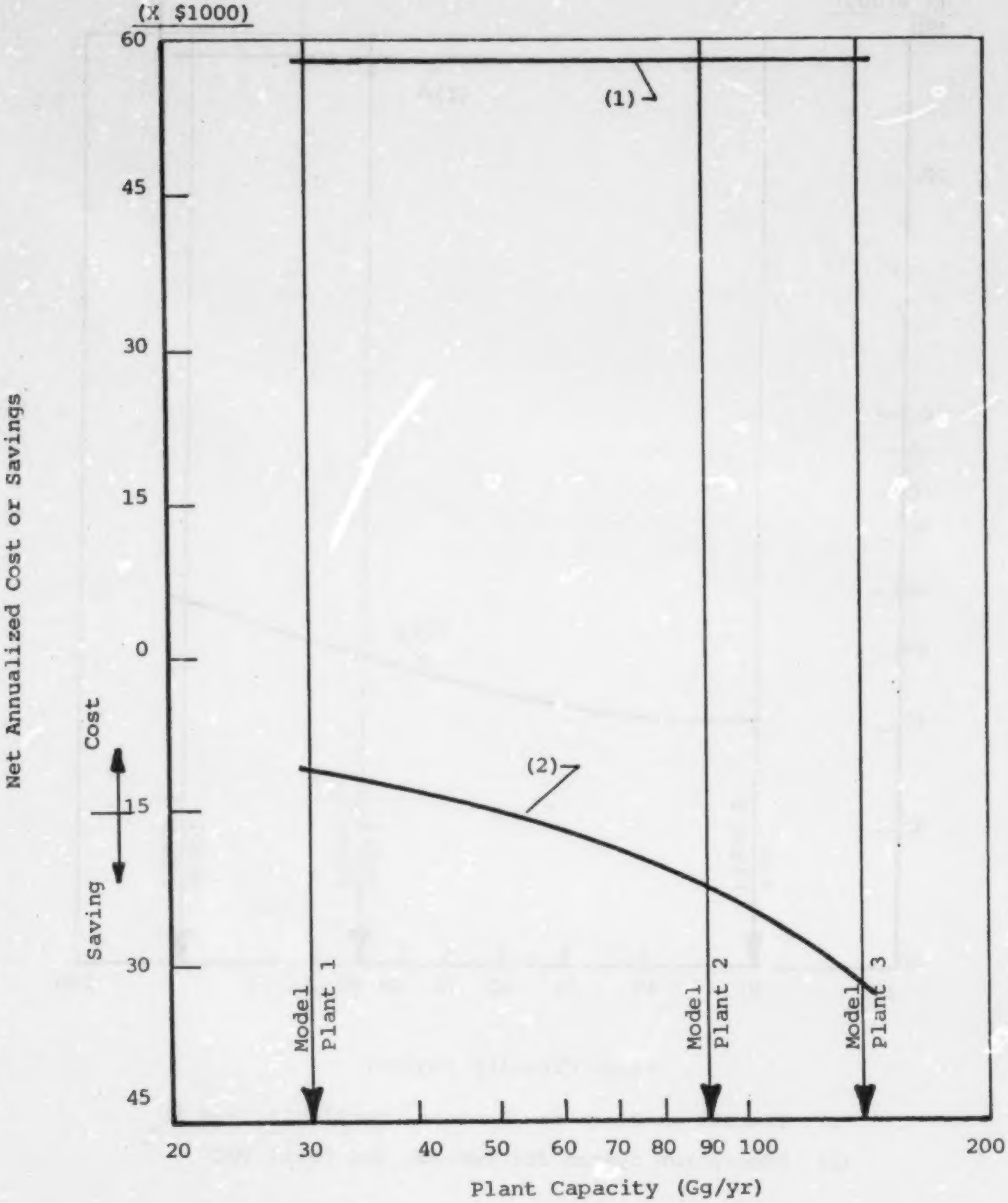


Plant Capacity (Gg/yr)

(1) Thermal oxidizer for benzene, total VOC, and NO_x

(2) Adsorption system for benzene and total VOC

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control



(1) Thermal oxidizer for benzene and total VOC.
(2) Absorption system for benzene and total VOC.

Fig. VI-2. Net Annual Cost or Savings vs Plant Capacity for Emission Control

C. REFERENCE*

1. D. G. Erikson, IT Enviroscience, Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC)

2. D. G. Erikson, IT Enviroscience, Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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VII. SUMMARY

All domestic nitrobenzene production is based on nitrating benzene with nitric acid mixed with sulfuric acid. Approximately 97% of all nitrobenzene produced is consumed in the manufacture of aniline.[1] The two chemicals are expected to grow at an average annual rate of about 7%.

Emission sources and control levels for the model plants are summarized in Table VII-1.

Projected emissions for the domestic nitrobenzene industry in 1979 are based on the following assumptions:

1. The 1978 production estimated in Sect. II increased by 7% during 1979 to 244,000 Mg.
2. The 90,000-Mg/yr model-plant emission rates, excluding fugitive emissions, are typical for the composite industry.
3. For the purpose of projecting fugitive emissions, the average number of pumps and valves for the seven domestic nitrobenzene manufacturing plants is the same as that for the model plants.

A weighted average of the following individual emission control estimates for process, in-process storage, raw material and product storage, secondary, and fugitive emissions indicates that the domestic nitrobenzene industry is approximately 50% controlled:

	Percent Controlled
Process emissions	50
In-process storage emissions	38
Raw material and product storage emissions	53
Secondary emissions	0
Fugitive emissions	80

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[1] T. C. Gunn and K. L. King, "Benzene," p. 618.5023V in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1977).

Table VII-1. Model Plant Emission Summary

	Emission Rate (kg/hr)											
	30,000-Mg/yr Model Plant				90,000-Mg/yr Model Plant				150,000-Mg/yr Model Plant			
	Uncontrolled		Controlled		Uncontrolled		Controlled		Uncontrolled		Controlled	
	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC	Benzene	Total VOC
Reactor and separator	3.29	3.30			9.86	9.91			16.4	16.5		
Waste-acid stripper	0.582	0.582	0.237[a]	0.267[a]	1.75	1.75	0.797[a]	0.0802[a]	2.91	2.91	1.32[a]	1.33[a]
Wash and neutralization	0.0277	0.0366			0.0832	0.110			0.139	0.183		
Nitrobenzene stripper	0.582	0.586	0.044[b]	0.044[b]	1.75	1.76	0.148[b]	0.149[b]	2.91	2.93	0.245[b]	0.274[b]
Small benzene storage	0.262	0.262			0.797	0.797			1.31	1.31		
Waste-acid storage	0.177	0.177			0.526	0.526			0.830	0.830		
Benzene storage	1.01	1.01	0.151	0.151	2.91	2.91	0.437	0.437	4.81	4.81	0.721	0.721
Nitrobenzene storage		0.0083		0.0083		0.0197		0.0197		0.031		0.031
Fugitive	6.5	10.2	1.70	3.70	6.5	10.2	1.70	3.70	6.5	10.2	1.70	3.70
Secondary	0.342	1.10	0.342	1.10	1.03	3.39	1.03	3.39	1.71	5.65	1.71	5.65
Total with vent absorber	12.8	17.3	2.43	5.23	25.2	31.4	3.96	8.32	37.5	45.4	5.45	11.43
Total with thermal oxidizer	12.8	17.3	2.24	5.01	25.2	31.4	3.32	7.70	37.5	45.4	4.38	10.35

[a] Controlled by vent absorber.

[b] Controlled by thermal oxidizer.

For the process, storage, and secondary emissions the projections are based on data reported from producers representing 83% of domestic capacity. The fugitive-emission projection is based on the estimate that all equipment handling nitrobenzene would be controlled because of the extreme toxicity of that material and the necessity for worker protection and that all equipment not handling nitrobenzene is uncontrolled in respect to the fugitive-emission calculations. From these data the emission projections for the domestic nitrobenzene industry in 1979 were 434 Mg of benzene and 619 Mg of total VOC.

The predominant emission points are the reactor and separator vent and the storage tanks. The emissions from the reactor and separator vent and other process emissions can be controlled in conjunction with emissions from the benzene daily-storage tank and from the waste-acid storage tank by a vent absorber using nitrobenzene as the absorbent or by a thermal oxidizer. These control devices result in removal efficiencies of 95% and 99% respectively. The capital cost of the vent absorber is $41,500, $48,000, and $56,500 for the 30,000-, 90,000-, and 150,000-Mg/yr model plants, respectively. Due to the small duty requirements, the thermal oxidizer capital cost is constant at $277,000 for all three model plant sizes. Benzene storage emissions from the main storage tanks can be controlled by using covered floating-roof tanks in a new plant or by retrofitting existing fixed-roof tanks with floating-roof tanks. The emission reductions resulting from the use of floating roof is 85% of the fixed-roof-tank emissions.

APPENDIX A

Table A-1. Physical Properties of Nitrobenzene and Benzene

	Nitrobenzene[a]	Benzene[b]
Synonyms	Oil of mirbane, nitrobenzol, mononitrobenzene, artificial oil of bitter almonds, solvent black 5, nigrosine spirit soluble B	Benzol, phenylhydride, coal naphtha
Molecular formula	$C_6H_5NO_2$	C_6H_6
Molecular weight	123.11	78.11
Physical state	Solid or oily liquid	Liquid
Vapor pressure	0.284 mm Hg at 25°C	95.9 mm Hg at 25°C
Vapor density	4.25	2.77
Boiling point	210.8°C at 760 mm Hg	80.1°C at 760 mm Hg
Melting point	5.7°C	5.5°C
Density	1.2037 g/ml at 20°C/4°C	0.8787 g/ml at 20°C/4°C
Water solubility	Slight (0.09 g/100 ml of H_2O at 20°C)[b]	Slight (1.79 g/100 ml of H_2O)

[a] Except for the last item, the data in this table are from: J. Dorigan *et al.*, *"Scoring of Organic Air Pollutants - Chemistry, Production, and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N),"* MTR-7248, Rev. 1, Appendix III, p. A-III-264, Mitre Corp., Metrek Division (September 1976).

[b] J. Dorigan *et al.*, *"Scoring of Organic Air Pollutants - Chemistry, Production, and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C),"* MTR-7248, Rev. 1, Appendix I, p. AI-102, Mitre Corp., Metrek Division (September 1976).

[c] H.P.L. Kuhn, W. J. Taylor, Jr., and P. H. Groggins, "Nitration," Chap. 4, p. 110, in *Unit Processes in Organic Syntheses*, edited by P. H. Groggins, 5th ed., McGraw-Hill, New York, 1958.

APPENDIX B

AIR-DISPERSION PARAMETERS

Table B-1. Air-Dispersion Parameters for 90,000-Mg/yr Nitrobenzene Model Plant

Source	Emission Rate (g/sec) Benzene	Emission Rate (g/sec) Total VOC	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled				
Reactors and separator	2.74	2.75	20	0.038	328	3.99×10^{-3}	3.5
Waste-acid stripper	0.486	0.486	20	0.025	305	9.67×10^{-4}	2.0
Wash and neutralization	0.0231	0.0306	11	0.031	318	2.83×10^{-3}	3.8
Nitrobenzene stripper	0.486	0.489	20	0.025	305	9.72×10^{-4}	2.0
Small benzene storage tank	0.221	0.221	7.3	7.0	293		
Waste-acid storage	0.146	0.146	9.8	7.7	318		
Benzene storage	0.808	0.808	12.2	17.2	293		
Nitrobenzene storage		0.0055	12.2	12.2	313		
Fugitive	1.81	2.83					
Secondary	0.286	0.942					
			Controlled				
Vent absorber	0.221	0.223	20	0.076	298	9.22×10^{-3}	2.0
Thermal oxidizer	0.0411	0.0411	20	0.305	477	1.88×10^{-1}	2.6
Benzene storage	0.121	0.121	12.2	17.2	293		
Nitrobenzene storage		0.0055	12.2	12.2	313		
Fugitive[a]	0.472	1.03			293-328		
Secondary	0.286	0.942					

[a] Distributed over an area of 40 m by 80 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE DETAILS AND CALCULATIONS

A. GENERAL

This appendix contains the details of the estimated costs presented in this report.

Capital costs shown are based on an accuracy range of +30% to -23%. This range is a function of the degree of detailed data available when the estimate was made. The evaluation made in this report is a screening study based on general design criteria, block flowsheets, approximate material balances, and general equipment requirements. Figure D-1 illustrates the relationship between the degree of accuracy of an estimated cost and the amount of data available. The allowance indicated on this chart to cover the undefined scope of the project has been included in the estimated costs.

This type of estimate is an acceptable basis to provide a screening estimate to indicate the most cost-effective alternative, within the limits of accuracy indicated.

B. ABSORPTION OF PROCESS EMISSIONS

Capital and operating cost estimates for the model-plant vent absorption systems described in Sect. V were determined as follows. The example given below is for model-plant 2 (90,000 Mg/yr capacity).

Basis:

Plant, 90,000-Mg/yr

Vent composition and rate, as follows:

Component	Rate (lb/hr)	Composition (wt %)
Benzene	34.47	29.0
Nitrobenzene	0.18	0.1
N_2	79.75	67.0
$NO_x(NO_2)$	3.28	2.8
H_2O	1.25	1.1
Total	118.93	100.0

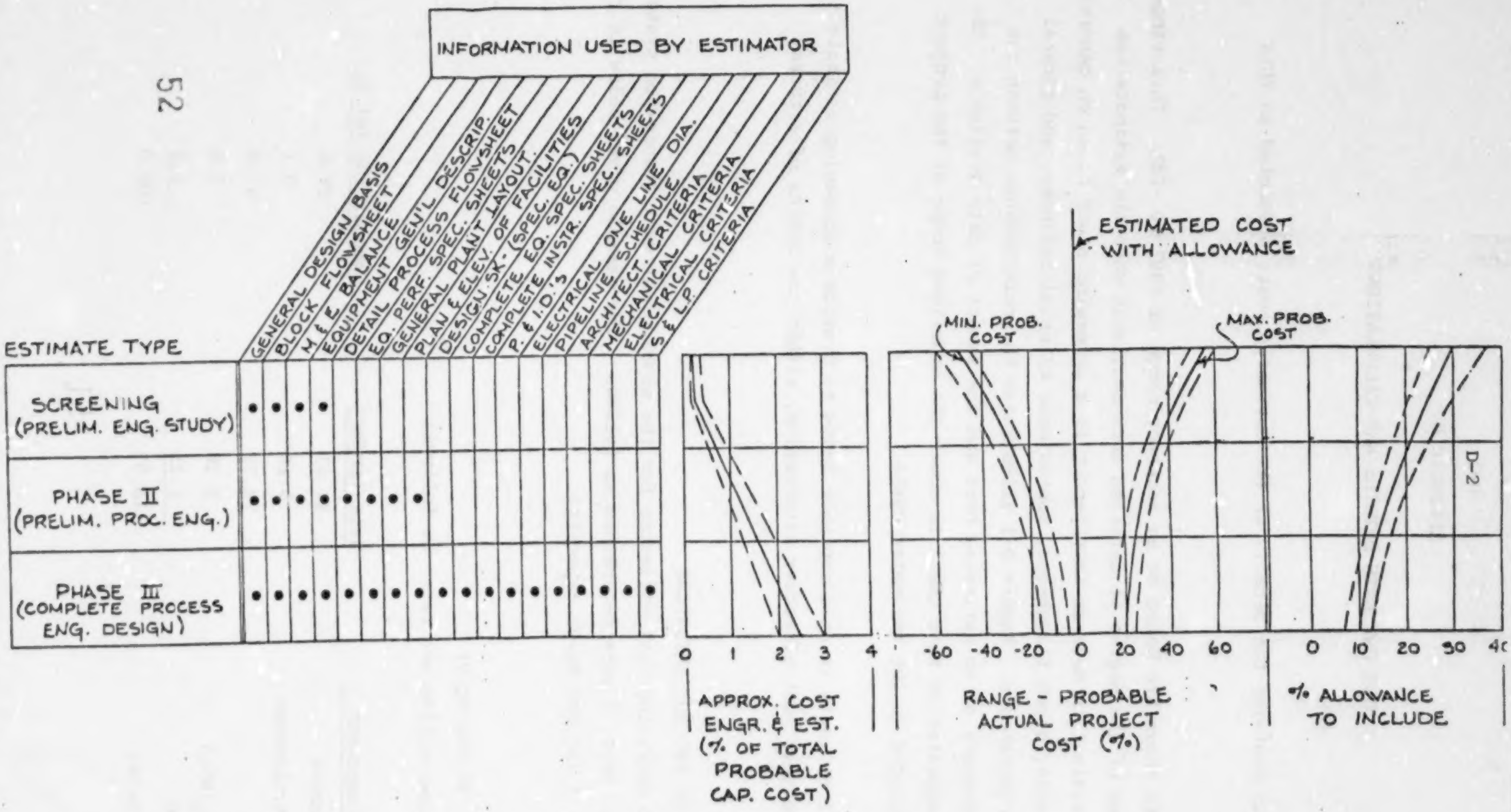

Fig. D-1. Precision of Capital Cost Estimates

LATEST REVISION - 5/2/77

The specified system consists of a packed tower with the necessary instruments and controls, a solvent feed pump, a refrigerated solvent cooler and the corresponding refrigeration equipment, a tower bottoms-discharge pump, and a blower to overcome tower pressure drop.

As designed the system uses nitrobenzene, chilled to 15°C, as the scrubbing solvent and existing process capability for the separation of the absorbed benzene by recycling the liquid bottoms stream from the absorber to an existing nitrobenzene stripper. It is assumed that the existing stripper capacity is sufficient to handle the additional load. Estimated control equipment costs would be increased if additional stripping capacity is required.

Following is a summary of the design parameters used to estimate the capital and operating costs. The absorber parameters were developed by standard design methods described by Treybal.[1]

Absorber tower, 10 in. dia, 15 ft packed height, 1/2-in. Raschig rings
Refrigeration, 1 ton at 15°C
Blower, 30 cfm, 8-in. WC
Pumps, 2 gpm
Solvent (nitrobenzene) rate, 452 lb/hr at 15°C
Steam (for stripping), 0.5 lb of steam/lb of stripper feed

Capital cost estimates were developed by the summation of installed costs for the major individual components of each system. These installed capital costs are based on IT Enviroscience experience, adjusted to a December 1979 base. On this basis the installed capital cost for the absorption system is estimated to be $48,000. The cost of utilities (stream and electrical power) is estimated to be $5700/yr, and the fixed cost is estimated to be $13,900/yr ($48,000 X 29%). With an estimated credit for recovered benzene of $28,600 ($0.10/lb) the absorption system would provide an estimated savings of $9000/yr.

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[1] R. E. Treybal, Mass-Transfer Operations, Chaps. 6 and 8, McGraw-Hill, New York, 1955.

C. INCINERATION OF PROCESS EMISSIONS

A preliminary estimate was made of the size and cost for a thermal oxidizer to incinerate the process VOC and NO_x emissions. The following design basis was used for the estimate:

Model-plant capacity	90,000 Mg/yr
Waste-gas composition (lb/hr)	
Benzene	34.47
NB	0.18
N_2	79.75
NO_x (NO_2)	3.28
H_2O	1.25
	118.93

238 acfm at 60°F (including combustion air)

225 scfm at 32°F

Waste gas fuel valve 47 Btu/scf

The incinerator system must include a small combustion chamber for reducing NO_x to N_2 by the waste-gas stream being burned in a reducing atmosphere, with less than theoretical air used for complete combustion. This chamber is followed by the main combustion chamber, where additional air is introduced to oxidize the organics. Some auxiliary fuel is required for flame stability, but the cost of the small quantity of fuel is relatively insignificant.

It is estimated that the first combustion chamber will operate at approximately 2000°F and the second chamber at approximately 1600°F, which are adequate for VOC destruction. The control device evaluation report for thermal oxidation[2] was used to determine the preliminary estimate for the thermal oxidizer. The cost estimates presented in the thermal oxidation report do not cover any thermal oxidizer sized to handle a waste-gas stream of less than 500 scfm, and none are designed with two combustion chambers. The 500-scfm incinerator was the smallest standard incinerator listed by any of the vendors contacted. For this preliminary estimate it is reasonable to assume that the cost of an incineratorator with two combustion chambers in series sized to handle a waste-gas stream of 225 scfm will be approximately the same as that for the smallest units quoted. Although for the smallest units the duty specifications do not have a large bearing on installed capital, the most appropriate duty specifications are listed on the table of p. B-21 of the thermal oxidation report.[2] On this basis the installed cost for the thermal oxidizer is estimated to be $277,000. The auxiliary fuel cost is considered to be negligible, the manpower requirement is estimated to be $18,000/yr, and the fixed cost is estmated to be $80,000/yr ($277,000 X 29%). The total annual operating cost is estimated to be $98,000.

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[2] J. W. Blackburn, IT Enviroscience, Control Device Evaluation. Thermal Oxidation Supplement (September 1980) (EPA/ESED report, Research Triangle Park, NC).

APPENDIX E

EXISTING PLANT CONSIDERATIONS

A. CURRENT INDUSTRY

Information on control devices used by nitrobenzene producers was secured from four producers for five nitrobenzene plants representing about 89% of the industry capacity.

1. Dupont, Beaumont, TX
   A water scrubber is used to control benzene-contaminated vent emission, and benzene storage emissions are controlled by use of a floating-roof tank. Streams of oxides of nitrogen contaminated with benzene are controlled by incineration. A refrigerated vapor condenser is used for control of emissions from the waste-acid tanks.[1]
2. Dupont, Gibbstown, NJ
   Streams of oxides of nitrogen contaminated with benzene are controlled by condensation and a benzene-contaminated vent emission is controlled by water scrubbing.[2]
3. First Mississippi, Pascagoula, MS
   An absorbing reactor, reported as being highly efficient, was initially utilized, but it was subsequently indicated that the reactor was converted to an absorption column, with nitrobenzene used as the scrubbing liquor, for control of all process emissions.[3]
4. Mobay, New Martinsville, WV
   No control devices were reported.[4]
5. Rubicon, Geismar, LA
   An absorption column in which nitrobenzene is used as the scrubbing liquor is used for control of all process emissions. A water scrubber is used for control of emissions from a benzene-contaminated vent.[5,6]

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of costs associated with this difficulty.it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant. An absorption control system using nitrobenzene as the absorbing liquor could be especially difficult to retrofit if existing nitrobenzene stripping capacity is insufficient for the increased demand.

E. REFERENCES*

1. C. W. Stuewe, IT Enviroscience, Trip Report on Visit to E. I. du Pont de Nemours & Co., Beaumont, TX, Sept. 7, 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
2. W. Smith, E. I. du Pont de Nemours & Co., letter to D. R. Goodwin, EPA, Feb. 3, 1978.
3. R. Barker, First Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 20, 1978.
4. L. P. Hughes, Mobay Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 31, 1978.
5. C. W. Stuewe, IT Enviroscience, Trip Report on Visit to Rubicon Chemicals, Geismar, LA, July 19, 20, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
6. W. C. Anthon, Rubicon Chemicals, letter to David A. Beck, EPA, Apr. 14, 1978.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 2

ANILINE

F. D. Hobbs
C. W. Stuewe

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

October 1980

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Aniline was selected for study because it is an important intermediate in the synthetic organic chemicals manufacturing industry (SOCMI) and has a relatively high production rate. The interrelationship between the manufacture of aniline and nitrobenzene also was a consideration. It is estimated that 97% of the nitrobenzene produced domestically is converted to aniline, as is cited in a previous report.[1] Nitrobenzene production results in emissions of significant amounts of benzene, a substance listed as a hazardous pollutant by the EPA (Federal Register, June 8, 1977). Aniline production also will create benzene emissions if benzene remains with the nitrobenzene feed as an impurity. Emissions of aniline itself are restricted because of its relatively low volatility (see Appendix A for pertinent physical properties of aniline).

B. USAGE AND GROWTH

The end uses and expected growth rates of aniline are given in Table II-1. The predominant use of aniline is as an intermediate in the manufacture of diphenylmethane diisocyanate (MDI) and its polymeric derivative polymethylenepolyphenyl isocyanate (PMPPI), which are important in the production of polyurethane foams.[2] The expected annual growth of 8% for this application of aniline could be higher if government regulations require certain standards for insulation in residential housing; on the other hand, it could be lower if a planned MDI plant based on nitrobenzene instead of aniline proves to be commercially successful.[3] Other uses of aniline[3] are as an intermediate in the production of rubber-processing chemicals, hydroquinone, pesticide intermediates, dyes, and pharmaceuticals.

The current domestic aniline capacity is reported to be about 528,000 Mg/yr (capacity increased about 153,000 Mg/yr during 1978 and 1979), with 1978 production utilizing about 53% of that capacity. The projected capacity will increase to about 567,000 Mg/yr by 1983, and, based on predicted growth rates, production will utilize about 66% of the capacity.[3]

Six producers were operating eight domestic aniline plants as of January 1, 1979. Table II-2 lists the producers and their capacities, and Fig. II-1 shows their locations. Several recent developments have affected the status of

Table II-1. Aniline Usage and Growth*

End Use	Percentage of Production (1978)	1978—1983 Average Rate Growth (%/yr)
Diphenylmethane diisocyanate (MDI)	52	8.0
Rubber chemicals	29	2.0—3.0
Dyes	4	3.0
Hydroquinone	3	4.5
Drugs, pesticides, and miscellaneous	12	6.0

*See ref 3.

Table II-2. Aniline Capacity[a]

Plant and Location	Capacity (Mg/yr as of 1979)
American Cyanamid, Bound Brook, NJ	27,000[b]
American Cyanamid, Willow Island, WV	23,000
Du Pont, Beaumont, TX	118,000[c]
Du Pont, Gibbstown, NJ	73,000[d]
First Chemical, Pascagoula, MS	115,000[e]
Mallinckrodt, Raleigh, NC	f
Mobay, New Martinsville, WV	45,000
Rubicon, Geismar, LA	127,000[g]
Total	528,000

[a] See ref 3.

[b] Capacity brought back on-stream during 1978.

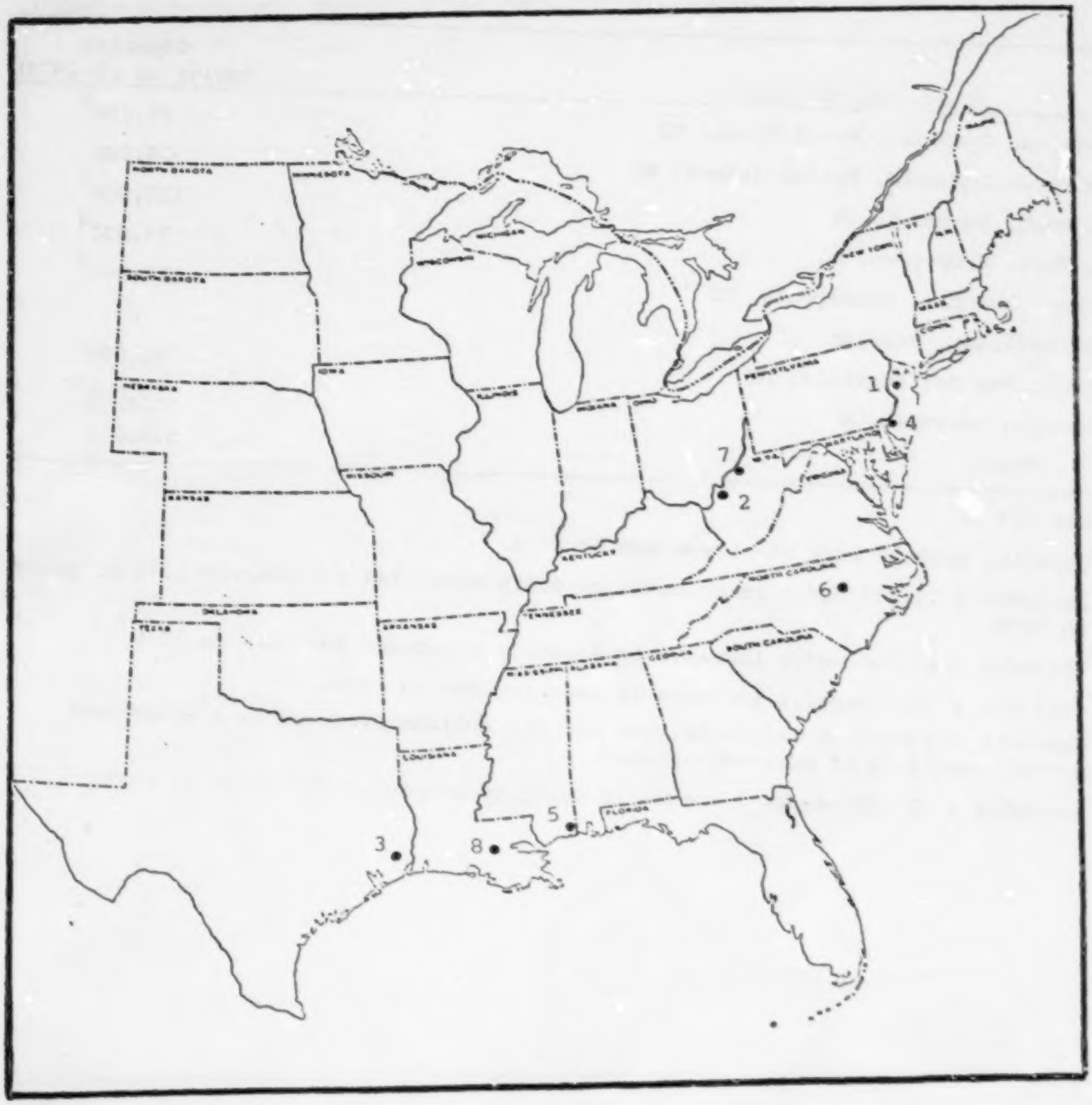
[c] Includes a 13,000-Mg/yr increase in capacity scheduled for late in 1978 or early in 1979.

[d] Includes a 13,000-Mg/yr increase in capacity scheduled for late in 1978.

[e] Includes a 70,000-Mg/yr increase in capacity during 1977.

[f] Capacity figures not available (see ref 4); aniline produced as a by-product in the synthesis of para-aminophenol.

[g] Includes a 100,000-Mg/yr increase in capacity scheduled for early in 1979.



1. American Cyanamid, Bound Brook,NJ
2. American Cyanamid, Willow Island, WV
3. Du Pont, Beaumont, TX
4. Du Pont, Gibbstown, NJ
5. First Chemical, Pascagoula, MS
6. Mallinckrodt, Raleigh, NC
7. Mobay, New Martinsville, WV
8. Rubicon, Geismar, LA

Fig. II-1. Aniline Manufacturing Locations

aniline capacity. American Cyanamid's plant at Bound Brook, NJ, had been on standby since 1974, but was brought back on-stream in 1978. The capacity of the American Cyanamid plant at Willow Island, WV, is to be increased by about 27,000 Mg/yr in early 1980. It was reported that the capacity of both du Pont plants was to be increased by 13,000 Mg/yr by late 1978 or early 1979. First Chemical increased its capacity by 70,000 Mg/yr in 1977. No capacity figures were located for the Mallinckrodt facility, where aniline is produced as a by-product of para-amenophenal. Rubicon scheduled an increase in aniline capacity of 100,000 Mg/yr for early 1979.[3—5]

An area of change in aniline production involves the methods of production. Most current domestic production of aniline is based on catalytic hydrogenation of vaporized nitrobenzene. However, it is reported[4] that a liquid-phase process is used commercially in the United States. The producer using this process was not identified. Also, it is reported that beginning in 1981 Mobay will recover aniline as a by-product from the production of iron oxide.[3] Also, a process based on the vapor-phase ammonolysis of phenol is used to produce aniline in the foreign market.[2] Since no further information has been obtained concerning these processes, they are not covered in this report.

C. REFERENCES*

1. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Nitrobenzene Product (in preparation for EPA, ESED, Research Triangle Park, NC).

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4. W. Löwenbach, J. Schlesinger, Nitrobenzene/Aniline Manufacture: Pollutant Prediction and Abatement, MTR-7828, Metrek Division of the MITRE Corp. (May 1978).

5. S. N. Robinson, Mallinckrodt, Inc., letter to Robert E. Rosenteel, EPA, July 28, 1980.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Vapor-phase hydrogenation of nitrobenzene is the predominant domestic method of aniline production, although liquid-phase hydrogenation is reported to be in current use. Also, one producer reportedly plans to begin recovering aniline from a process involving reaction of iron with nitrobenzene in the presence of a hydrochloric acid catalyst.[1] This process will yield aniline as a by-product of the iron oxide product.[1] Ammonolysis of chlorobenzene was once a significant route to aniline, but no current domestic aniline production is based on this process. Ammonolysis of phenol is used by foreign aniline producers.[2] This report presents details of the process based on vapor-phase hydrogenation of nitrobenzene, the predominant domestic method of aniline production.

B. NITROBENZENE HYDROGENATION PROCESS

The vapor-phase hydrogenation of nitrobenzene is accomplished by the use of a metal catalyst such as copper on a carrier according to the reaction

$$\underset{\text{(nitrobenzene)}}{C_6H_5NO_2} + \underset{\text{(hydrogen)}}{3H_2} \xrightarrow[\text{(copper)}]{\text{Cu}} \underset{\text{(aniline)}}{C_6H_5NH_2} + \underset{\text{(water)}}{2H_2O}$$

The flow diagram shown in Fig. III-1 represents a typical continuous process. Nitrobenzene (stream 1) is vaporized and fed with 300% excess hydrogen (stream 2) to a fluidized-bed reactor, which is held at about 270°C. Excess heat from the exothermic reaction is removed by internal cooling coils in the reactor. Product gases are filtered free of catalyst by internal filters in the top of the reactor. Product gases (stream 3) are passed through a condenser. Condensed materials (stream 4) are sent to a decanter, and noncondensables (stream 5) are recycled to the reactor. Condensables form two phases in the decanter: a lower phase (stream 6), which is crude aniline containing about 0.5% nitrobenzene and 5% water, and an upper aqueous phase (stream 7). The crude aniline phase is passed to a dehydration column that operates under vacuum. The aniline in the upper aqueous phase is recovered either by stripping or by extraction with nitrobenzene for recycle while the water is sent to wastewater treatment. Overheads from the dehydration column (stream 8) are condensed and recycled to the decanter. The bottoms (stream 9), which contain the aniline, are sent to the purification

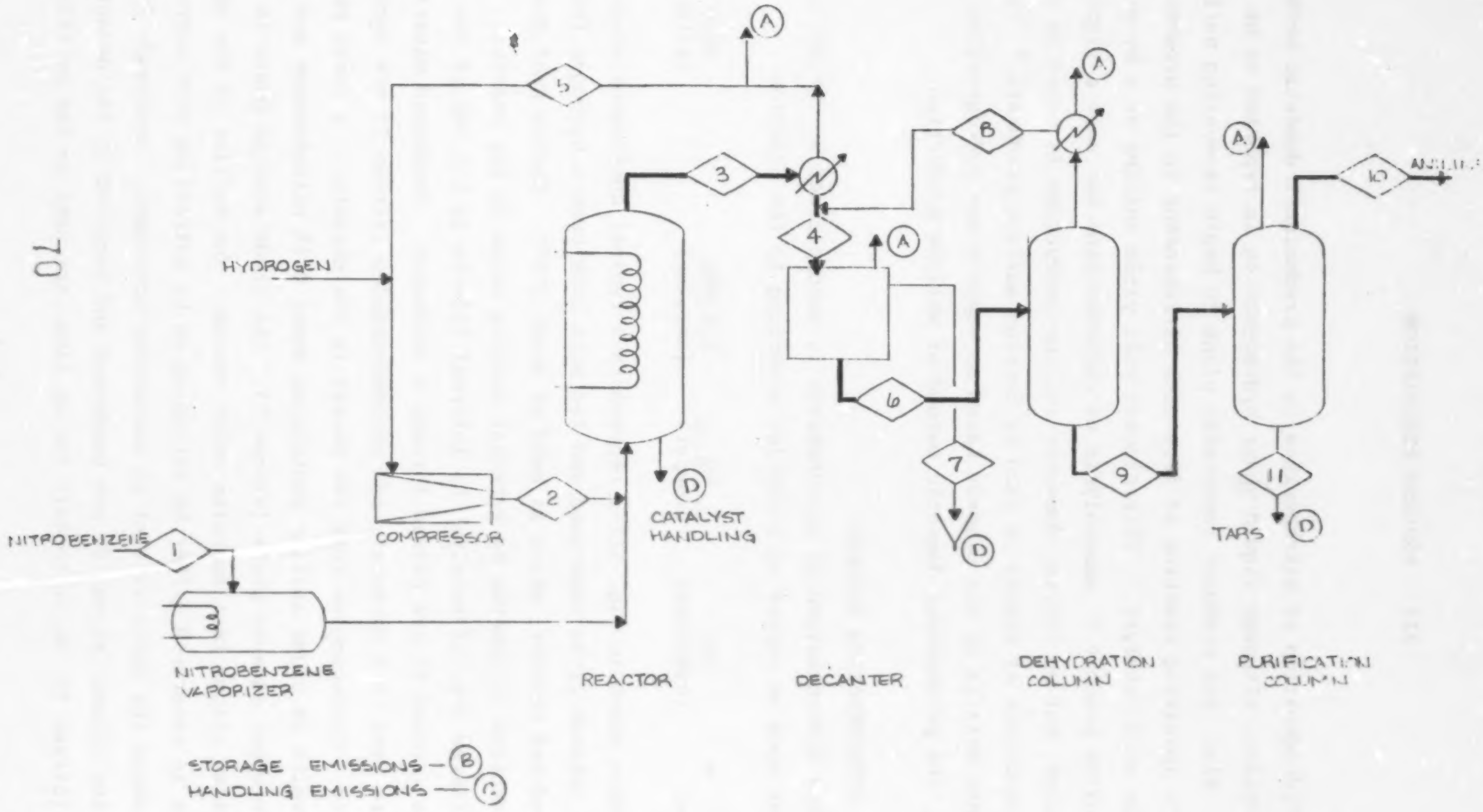
HYDROGEN
NITROBENZENE
1
2
3
4
5
6
7
8
9
10
11
A
D
ANILINE
TARS
COMPRESSOR
CATALYST HANDLING
NITROBENZENE VAPORIZER
REACTOR
DECANTER
DEHYDRATION COLUMN
PURIFICATION COLUMN
STORAGE EMISSIONS — B
HANDLING EMISSIONS — C

Fig. III-1. Process Flow Diagram for Manufacture of Aniline

column. The column operates under vacuum. Overheads (stream 10) from the purification column consist of product aniline. The bottoms (stream 11) are tars, which are disposed of.[3,4]

Process emissions typically would originate from the purge of noncondensables (Stream 5) during recycle to the reactor and from purge of inert gases from the various items of separation and purification equipment (vents A).[4]

Fugitive emissions of nitrobenzene and aniline can occur when leaks develop in valves, pump seals, and other equipment.

Storage emissions occur from tanks storing intermediate materials, final-product aniline, and waste materials. Handling emissions occur from transfer of product aniline for off-site shipment.

Potential sources of secondary emissions (D on Fig. III-1) are spent-catalyst, wastewater, and tars.

C. PROCESS VARIATIONS

The following variations of the process shown in Fig. III-1 are possible:

1. filtering catalyst fines from the product gases outside the reactor for recycle of the catalyst,
2. using a nickel sulfide catalyst deposited on alumina in a fixed-bed reactor,
3. using liquid-phase processing with different catalysts,
4. purifying the crude aniline from the decanter (stream 6, Fig. III-1) by first taking aniline and water overhead in a column, with heavies such as nitrobenzene being removed in the column bottoms; the overheads would then be distilled to separate the product aniline from water.[5]

Of these variations it is known that removal of catalyst from product gases outside the reactor can have a significant influence on process emissions, as is described in Sect. IV of this report. No information is available for differences in emissions resulting from other variations. However, it is believed that approximately 80% of the aniline currently produced in the United States is manufactured by a process that is basically similar to the process described in Sect. III-B of this report. Therefore the emissions discussed in Sect. IV should accurately represent current practices.

As was mentioned previously, ammonolysis of phenol is used by foreign producers to manufacture aniline. No information is available on emissions from this process for comparison to those from the vapor-phase hydrogenation of nitrobenzene process.

D. REFERENCES*

1. E. M. Klapproth, "CEH Product Review on Aniline and Nitrobenzene," pp. 614.5030A—I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1979).

2. M. Gans, "Which Route to Aniline?," Hydrocarbon Processing 55(11), 145—150 (November 1976).

3. F. A. Lowenheim and M. K. Moran, Faith, Keyes, & Clark's Industrial Chemicals, 4th ed., pp. 113 and 114, Wiley-Interscience, New York, 1975.

4. C. W. Stuewe, IT Enviroscience, Inc., Trip Report on Visit to E. I. du Pont de Nemours & Co, Beaumont, TX, Sept. 7, 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. W. Löwenbach and J. Schlesinger, Nitrobenzene/Aniline Manufacture: Pollutant Prediction and Abatement, MTR-7828, Metrek Division of the MITRE Corp. (May 1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

A. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing oxone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to oxone formation.

As is indicated on Fig. III-1, several process vents (vents A) are used to purge inert gases from the production equipment. The uncontrolled total VOC process emissions listed in Table IV-1 were calculated for a 100,000-Mg/yr production plant at full capacity from information supplied by producers. The total process emissions in Table IV-1 are a capacity-weighted average of the emissions reported by producers. The benzene emissions were calculated from data reported by one producer.[1] A process variation that can significantly influence process emissions is the manner in which the catalyst is handled. One producer reports filtration of catalyst fines from the reaction gases outside the reactor for recycle. This operation is reported[1] to create an uncontrolled emission of 1.4 kg of VOC per Mg of production. Another manufacturing location reports[2] emissions from catalyst handling to be 0.018 kg of VOC per Mg of production. However, in the latter case it is not known whether the catalyst handling is for recycle of the catalyst or for disposal of spent catalyst. Emissions from disposal of spent catalyst would be classified as a secondary emission source.[1—3]

The storage emissions shown in Table IV-1 are a combination of reported emissions from storage of crude aniline and waste materials[2] and of calculated emissions based on the estimated use of two aniline product day tanks and one final aniline product tank. The calculations for emissions from these aniline tanks were based on equations from AP-42,[4] although breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[5] Emissions from loading aniline product into tank cars and trucks based on submerged loading into clean vessels were calculated with equations from AP-42.[4]

Table IV-1. Uncontrolled[a] Process, Storage, and Handling Emissions from a 100,000-Mg/yr Aniline Process Plant

		Uncontrolled Emissions			
		Ratio (kg/Mg)[b]		Rate (kg/hr)[c]	
Emission Source	Stream Designation (Fig. III-1)	Benzene	Total VOC	Benzene	Total VOC
Process vents	A	0.0057[d]	0.095[e]	0.065[d]	1.08
Storage	B		0.023		0.26
Handling	C		0.0012		0.014

[a] Emissions from plants employing no controls other than those necessary for economical operation.

[b] kg of emission per Mg of aniline produced.

[c] Based on 8760 hr/yr operation. Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[d] See ref 1.

[e] See refs 1—3.

As shown in Fig. III-1, there are three potential sources of secondary emissions: spent-catalyst handling, wastewaters, and tars from the purification column.

Secondary emissions and fugitive emissions were not estimated for this abbreviated report. Storage and handling, fugitive, and secondary emissions for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.[6—8]

B. REFERENCES*

1. D. W. Smith, E. I. du Pont de Nemours & Co., letter to D. R. Goodwin, EPA, Feb. 3, 1978.

2. C. W. Stuewe, IT Enviroscience, Inc., Trip Report for Visit to E. I. du Pont de Nemours & Co., Beaumont, TX, Sept. 7, 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. R. Barker, First Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 20, 1978.

4. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-1—4.3.12 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed (August 1977).

5. E. C. Pulaski, TRW, Inc., letter dated May 30, 1979, to Richard Burn, EPA.

6. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

7. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

8. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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V. APPLICABLE CONTROL SYSTEMS

A. EMISSION CONTROL OPTIONS

Various control devices can be used for control of emissions from process, storage, and secondary sources. Industry reports the control options currently in use to be condensation, water scrubbing, dilute sulfuric acid scrubbing, and thermal oxidation.[1—5] Condensation is used for control of emissions from distillation,[1,3] from catalyst filtration and recycle,[2] and from storage.[3] Water scrubbing is used to control process and storage sources.[3,4] Thermal oxidation is used to control emissions from the reactor purge vent[1,4] and secondary sources.[4] Additional details are provided in Appendix B.

It is estimated that aniline process emissions account for less than 0.002% of the total SOCMI emissions. Emissions from the aniline process are estimated to be relatively low because of the low volatility of the materials involved and the control devices already in use. Benzene emissions can occur from the production of aniline only as a result of benzene impurities contained in the nitrobenzene fed to the process.

B. REFERENCES*

1. C. W. Stuewe, IT Enviroscience, Inc., Trip Report for Visit to E. I. du Pont de Nemours & Co, Beaumont, TX, Sept. 7, 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
2. D. W. Smith, E. I. du Pont de Nemours & Co., letter to D. R. Goodwin, EPA, Feb. 3, 1978.
3. L. P. Hughes, Mobay Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 31, 1978.
4. W. L. Anthon, Rubicon Chemicals Inc., letter to D. A. Beck, EPA, Apr. 14, 1978.
5. S. N. Robinson, Mallinckrodt, Inc., letter dated July 28, 1980, to Robert E. Rosensteel, EPA.

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VI. SUMMARY

A. INDUSTRY CAPACITY AND ESTIMATED PRODUCTION

As is shown in Sect. II of this report, six domestic aniline producers were operating eight plants as of January 1, 1979. These producers have a listed capacity of 528,000 Mg/yr, although no capacity figure was located for the Mallinckrodt plant in Raleigh, NC. As is also shown in Sect. II, industry production was about 280,000 Mg in 1978. Based on an annual growth rate of 6%, the 1979 production was estimated to have been 297,000 Mg.

B. ESTIMATED EMISSIONS

Current process emissions were estimated by calculating a capacity-weighted average emissions ratio from information supplied by three producers[1—3] and multiplying that emission ratio times the estimated 1979 production listed above. This calculation indicates a total 1979 process emission of about 26 Mg of total VOC, which includes about 2 Mg of benzene. Storage, secondary, and fugitive emissions are not included in this estimate. Current process emission control devices reported to be in use by industry are described in Appendix B.

C. REFERENCES*

1. C. W. Stuewe, IT Enviroscience, Inc., Trip Report for Visit to E. I. du Pont de Nemours & Co., Beaumont, TX, Sept. 7, 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. D. W. Smith, E. I. du Pont de Nemours & Co., letter to D. R. Goodwin, EPA, Feb. 3, 1978.

3. W. L. Anthon, Rubicon Chemicals Inc., letter to D. A. Beck, EPA, Apr. 14, 1978.

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APPENDIX A

Table A-1. Physical Properties of Aniline*

Synonyms	Benzeneamine, benzamine, aminobenzine, phylamine, aminophen, aniline oil
Molecular formula	C_6H_7N
Molecular weight	93.12
Physical state	Liquid
Vapor pressure	0.67 mm Hg at 25°C
Vapor density	3.22
Boiling point	184°C
Melting point	-6.3°C
Density	1.02173 at 20°C/4°C
Water solubility	36.5 g/liter of H_2O

*J. Dorigan et al., Scoring of Organic Air Pollutants—Chemistry, Production and Toxicity of Selected Synthetic organic Chemicals (Chemicals A—C), MTR 7248, Rev. 1, Appendix, I, p. AI-78, MITRE Corp., Metrek Division (September 1976).

APPENDIX B

EXISTING PLANT CONSIDERATIONS

A. EXISTING PLANT CONSIDERATIONS

Table B-1[1—6] lists process control devices reported in use by industry. As is described in the table, many of the control devices are also used for control of storage and/or secondary sources.

B. RETROFITTING CONTROLS

As is described in Sect. III of this report, numerous variations of the process for production of aniline are possible. Some of these variations influence the amount and rate of the emissions. For example, filtration of catalyst from reaction gases outside the reactor for recycle creates a significant emission source, as is described in more detail in Sect. IV. Such variations and the resulting influence on emissions should be considered before it is decided to retrofit control devices into existing plants.

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

Table B-1. Process Control Devices Used by Industry[a]

Producer and Location	Devices	Percentage Control	Controlled Process Emissions Rate (kg/Mg)[b]
Du Pont, Beaumont, TX[c]	Condenser[d]	NR[e]	0.014
	Thermal oxidation[f]	NR[e]	NR[e]
Du Pont, Gibbstown, NJ[g]	Condenser[h]	96	0.056
First Chemical Corp., Pascagoula, MS[l]	None reported		
Mobay Chemical Co., New Martinsville, WV[j]	Condensers[k]	NR[e]	NR[e]
	Water scrubber	NR[e]	NR[e]
Rubicon Chemical, Geismar, LA[i]	Water scrubber[m]	99.9	0.001[n]
	Thermal oxidizer[o]	p	0.38[n]
Malinckrodt, Raleigh, NC	Dilute sulfuric acid scrubber	NR[e]	NR[e]

[a] Devices listed specifically for control of secondary emissions are not included here but are listed in Section V of this report.

[b] kg of emission per Mg of reported capacity for the specific controlled emissions.

[c] See ref 1.

[d] Condenser on two distillation vents.

[e] Not reported or too little information available for calculation.

[f] Reactor vented to combustion device; no information given for efficiency or final emissions.

[g] See ref 2.

[h] The condenser is reported to control emissions from purging a catalyst filtration and recycle operation. Vacuum-pump liquid-ring seals also are reported to be used on 3 distillation columns to reduce emissions and were judged to be normal items of equipment; disposal route for the liquid is not described.

[i] See ref 3.

[j] See ref 4.

[k] Process and storage emissions are controlled separately by condensers and combined for control by a water scrubber.

[l] See ref 5.

[m] A scrubber is used to control combined storage and process emissions.

[n] The production rate used to calculate the emission ratio was not specified (see ref 5); thecapacity of the facility at the time that the referenced data were prepared was used for the calculations given here.

[o] The thermal oxidizer controls emissions from the reactor purge vent and also is used for treatment of catalyst and other wet and solid wastes, which are secondary sources.

[p] The overall efficiency for the combined process and secondary sources is reported to be greater than 99 percent.

C. REFERENCES*

1. C. W. Stuewe, IT Enviroscience, Inc., Trip Report for Visit to E. I. du Pont de Nemours & Co, Beaumont, TX, Sept. 7, 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. D. W. Smith, E. I. du Pont de Nemours & Co., letter to D. R. Goodwin, EPA, Feb. 3, 1978.

3. R. Barker, First Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 20, 1978.

4. L. P. Hughes, Mobay Chemical Corp., letter to D. R. Goodwin, EPA, Jan. 31, 1978.

5. W. L. Anthon, Rubicon Chemicals Inc., letter to D. A. Beck, EPA, Apr. 14, 1978.

6. S. N. Robinson, Mallinckrodt, Inc., letter dated July 28, 1980, to Robert E. Rosensteel, EPA.

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REPORT 3

CUMENE

C. A. Peterson

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

December 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION[1]

Cumene production was selected for study because it is an aromatic chemical that consumes benzene in its production; it is known that benzene causes harmful health effects;[2] and the pattern of rapid industrial growth to high production levels indicates that large quantities of benzene are being handled and consumed.

Benzene is present at relatively high levels in many of the process streams during cumene manufacture; so vents and other emission sources are likely to discharge significant amounts of benzene vapors to the air unless appropriate emission control techniques are used.

B. CUMENE USAGE AND GROWTH[1,3]*

Table II-1 shows cumene production and growth rate. The predominant (99%) use for cumene is in the manufacture of phenol and acetone by the cumene hydroperoxide process. Small amounts of α-methylstyrene and acetophenone are also made from cumene, usually as by-products from the cumene hydroperoxide process. In the period from 1955 to 1975 the cumene hydroperoxide process grew to dominance as the principal route used to manufacture phenol (and the co-product acetone). In 1955, only 13% of the total domestic phenol and 8% of the domestic acetone were manufactured from cumene. By 1975 these percentages had risen to 88% for domestic phenol and 58% for domestic acetone.

Some cumene is sold on the open market to processors for conversion to phenol and acetone, but a large share of the total cumene manufactured is further processed to phenol and acetone by large, integrated producers that manufacture cumene for use as an intermediate in their manufacturing complex. Because of this large internal consumption of cumene by integrated producers, the data on production of cumene shown in Table II-1 are expected to contain some inaccuracies, but these figures are the best numbers available. The current projected growth rate of 4.4% is expected to continue through 1982.

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*In order to minimize the revision time, the data used for the original draft of this report have been retained. For our purposes the change in usage and growth data is not believed to be significant.

Table II-1. Cumene Production and Growth*

Year	Production Rate (Gg/yr)	Growth Rate (%/year)
1956	72	
1957	77	
1958	80	
1959	97	15.3
1960	99	
1961	133	
1962	175	
1963	196	
1964	249	
1965	301	
1966	406	
1967	514	24.3
1968	611	
1969	765	
1970	899	
1971	972	
1972	1040	
1973	1209	
1974	1318	4.3
1975	908	
1976	1197	
1977	1197	
1978	1257	
1982	1492 (est.)	4.4 (est.)

*Data for 1956 to 1976 from ref 1, p. 638.5030F; data for 1977 through 1982 from ref 3.

C. DOMESTIC PRODUCERS[1,3—14]

As of 1978, twelve producers of cumene in the United States were operating plants at thirteen locations. Table II-2 lists the producers, plant capacity, and (where known) the type of catalyst system used in the plant. Figure II-1 shows the locations of the 13 operating plants.

Marathon Oil Company has shut down their plant at Texas City, TX, which was rated at a production capacity of 95.2 Gg/yr, and has indicated that they do not intend to resume manufacture of cumene in this facility.[4] Costal States Petrochemical Company has converted their 64-Gg/yr cumene facility at Corpus Christi, TX, to manufacture other products.[12] The rated capacity of operating plants in the United States is estimated at a total of 2193.6 Gg/yr (Table II-2). The 1978 production was 1257 Gg (57% of capacity), and the estimate for 1982 production of 1492 Gg is only 68% of the rated capacity (Table II-1). Two new, large plants have recently been started up: Shell's 317.5-Gg/yr plant at Deer Park, TX (1977),[3] and Georga Pacific's 340.1-Gg/yr plant at Houston, TX (1978).[11] With these two new, large plants operating and with present and predicted operating levels far below total plant capacity, it is expected that additional older, smaller plants for manufacture of cumene will be shut down.

Table II-2. Cumene Production Capacity, 1978

Company and Plant Location	Capacity (Gg/yr)	Catalyst System Type
Amoco Oil Co., Texas City, TX	13.6[a]	Unknown
Ashland Oil Co., Catlettsburg, KY	181.4[b]	Solid phosphoric acid
Chevron Oil Co., El Segundo, CA	40.8[a]	Unknown
Clark Oil Co., Blue Island, IL	54.4[a]	Unknown
Georgia Pacific Corp., Houston, TX	340.1[c]	Solid phosphoric acid[b]
Getty Oil Co., El Dorado, KS	61.2[a]	Unknown
Gulf Oil Co., Philadelphia, PA	204.1[a]	Solid phosphoric acid[b]
Gulf Oil Co., Port Arthur, TX	200.5[b]	Solid phosphoric acid
Monsanto Chemical Co., Chocolate Bayou, TX	317.5[b]	Solid phosphoric acid
Shell Oil Co., Deer Park, TX	317.5[a]	Solid phosphoric acid
Sun Petroleum Products Co., Corpus Christi, TX	104.3[b]	Solid phosphoric acid
Texaco, Inc., Westville, NJ	68.0[a]	Unknown
Union Carbide Corp., Ponce, PR	290.2[b]	Aluminum chloride
Total	2193.6[d]	

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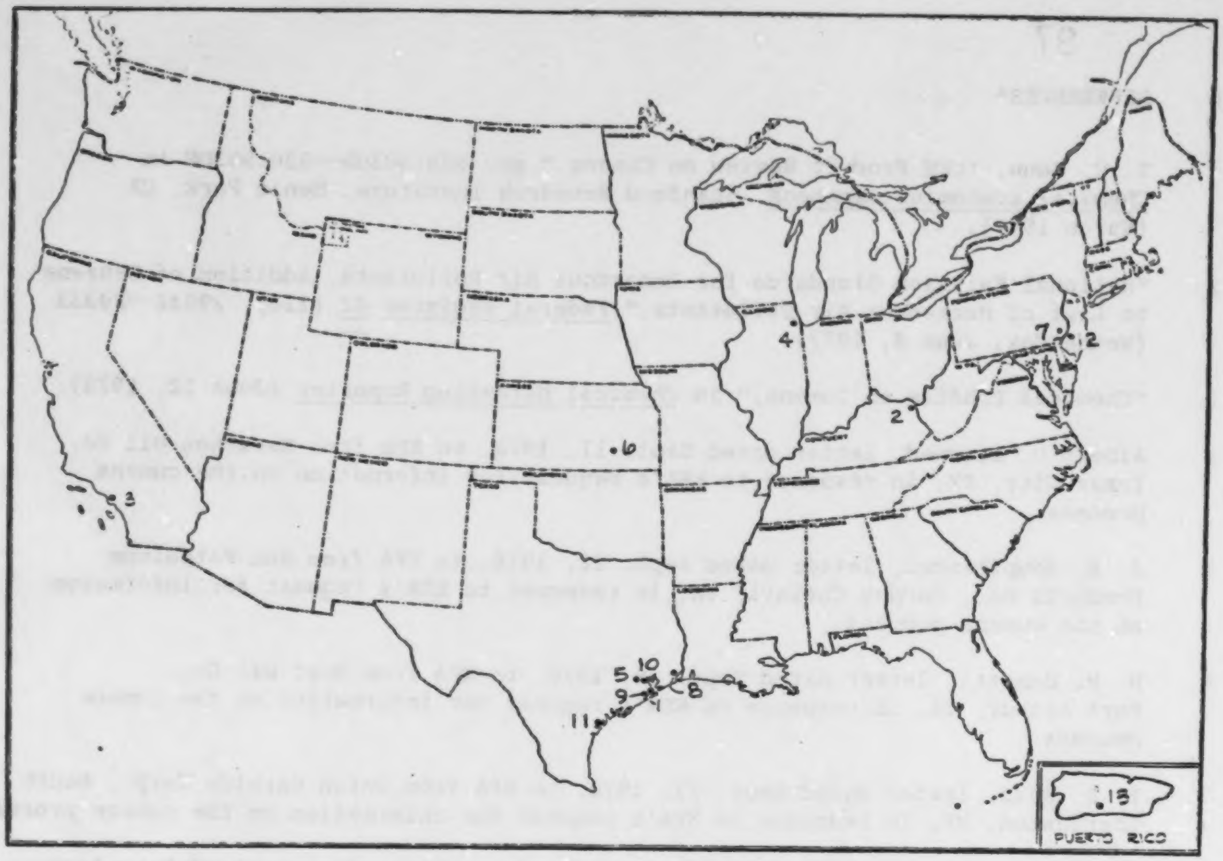
[a] From ref 3.

[b] From individual company replies to EPA in response to their request for information on cumene production.

[c] From ref 11.

[d] Champlin Petroleum Co. is building a 181-Gg/yr plant at Corpus Christi, TX, with completion scheduled for 1980; see ref 12.



1. Amoco Oil Co., Texas City, TX
2. Ashland Oil Co., Catlettsburg, KY
3. Chevron Oil Co., El Segundo, CA
4. Clark Oil Co., Blue Island, IL
5. Georgia Pacific Corp., Houston, TX
6. Getty Oil Co., El Dorado, KS
7. Gulf Oil Co., Philadelphia, PA
8. Gulf Oil Co., Port Arthur, TX
9. Monsanto Chem. Co., Chocolate Bayou, TX
10. Shell Oil Co., Deer Park, TX
11. Sun Petroleum Products Co., Corpus Christi, TX
12. Texaco, Inc., Westville, NJ
13. Union Carbide Corp., Ponce, PR

Fig. II-1. Locations of Plants Manufacturing Cumene

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D. REFERENCES*

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2. "National Emission Standards for Hazardous Air Pollutants, Addition of Benzene to List of Hazardous Air Pollutants," Federal Register 42 (110), 29332—29333 (Wednesday, June 8, 1977).

3. "Chemical Profile on Cumene," in Chemical Marketing Reporter (June 12, 1978).

4. Albert O. Learned, letter dated Sept. 11, 1978, to EPA from Marathon Oil Co., Texas City, TX, in response to EPA's request for information on the cumene process.

5. J. R. Kampfhenkel, letter dated Sept. 12, 1978, to EPA from Sun Petroleum Products Co., Corpus Christi, TX, in response to EPA's request for informaton on the cumene process.

6. M. P. Zanotti, letter dated Sept. 19, 1978, to EPA from Gulf Oil Co., Port Arthur, TX, in response to EPA's request for information on the cumene process.

7. F. D. Bess, letter dated Sept. 21, 1978, to EPA from Union Carbide Corp., South Charleston, WV, in response to EPA's request for information on the cumene process.

8. Oliver J. Zandona, letter dated Sept. 25, 1978, to EPA from Ashland Petroleum Co., Ashland, KY, in response to EPA's request for information on the cumene process.

9. Michael A. Pierle, letter dated Oct. 23, 1978, to EPA from Monsanto Chemical Co., St. Louis, MO, in response to EPA's request for information on the cumene process.

10. Attachment II, Information on the Cumene Process, from Shell Oil Co., Deer Park, TX, in response to EPA's request for information on the cumene process.

11. "Cumene Plant Operating at Georgia-Pacific Site," pp. 7, 49 in Chemical Marketing Reporter (Feb. 12, 1979).

12. S. A. Al-Sayyari and Koon-Ling Ring, "Cumene," pp 638.5030A—638.5030Q in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (March 1979).

13. J. B. Ellsworth, Georgia-Pacific Corp., letter dated Feb. 26, 1980, to J. R. Farmer, EPA, with information on catalyst type used.

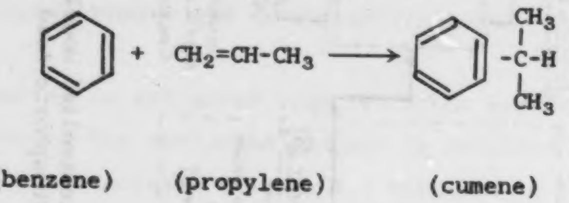
14. G. J. Wilson, Jr., Gulf Oil Co., U.S., letter dated Dec. 21, 1979, to J. R. Farmer, EPA, with comments on draft Cumene report.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION[1]

In the United States at present all chemical-grade cumene is manufactured by the alkylation of benzene with propylene. Benzene and propylene are reacted at elevated temperatures and pressures in the presence of an acidic catalyst. Excess benzene is used to minimize the formation of dialkylated or polyalkylated benzenes. The catalysts used may be solid phosphoric acid (on a catalyst support, such as alumina), aluminum chloride, or sulfuric acid. The reaction is exothermic. Process yields are about 94%, based on the amount of benzene consumed, and about 92%, based on the amount of propylene consumed. A simplified formula for this reaction is as follows:



B. CATALYSIS[2]

The selection of a catalyst system for the alkylation of benzene to cumene is the most important choice that affects plant design, raw-material purity requirements, number of processing steps, material of construction constraints, emission locations, and potential process emission quantities.

1. Solid Phosphoric Acid Catalyst[3]

Figure III-1 is a typical flowsheet for the manufacture of cumene by the process using phosphoric acid on a catalyst support (such as alumina). This is the most favored catalyst system. Basic process patents are held by UOP, Inc., Institute Francais du Petrole, and Bayer A.G.[1] Solid phosphoric acid is a selective catalyst that promotes the alkylation of benzene with propylene in a vapor-phase system that operates at about 205°C and 3.5×10^6 Pa.

Since the catalyst is selective, propylene feedstock for cumene manufacture does not have to be thoroughly refined before use. Crude propylene streams (1) from refinery crackers that are fractionated to about 70% propylene can be used in this process without further purification. After the propylene is consumed,

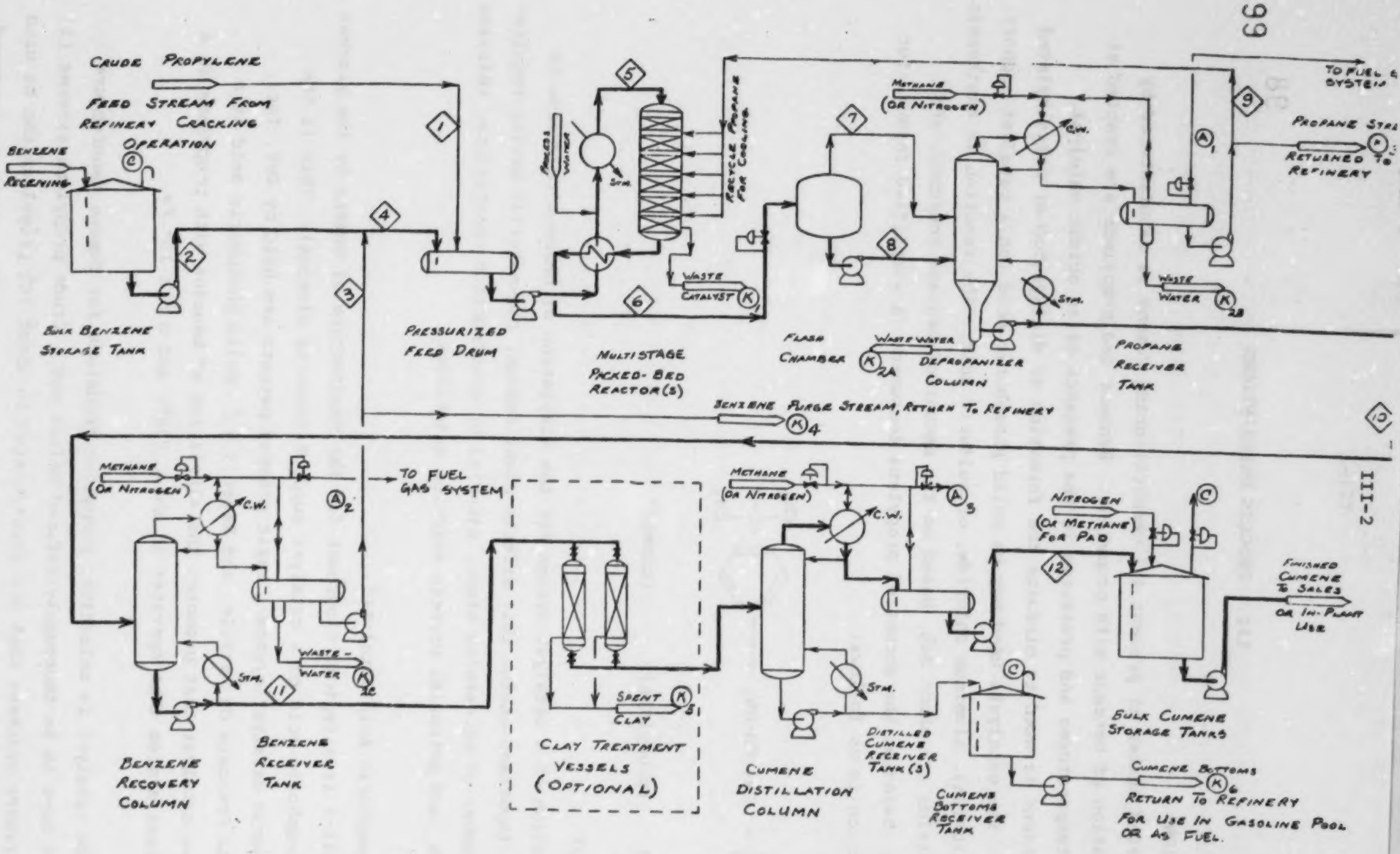

Crude Propylene
Feed Stream From Refinery Cracking Operation
Benzene Receiving
Bulk Benzene Storage Tank
Pressurized Feed Drum
Process Water
Stm.
Multistage Packed-Bed Reactor(s)
Recycle Propane For Cooling
Waste Catalyst
Flash Chamber
Waste Water
Depropanizer Column
Methane (Or Nitrogen)
C.W.
Propane Receiver Tank
Waste Water
To Fuel & System
Propane Str
Returned To Refinery
Benzene Purge Stream, Return To Refinery
To Fuel Gas System
Benzene Recovery Column
Benzene Receiver Tank
Waste-Water
Spent Clay
Clay Treatment Vessels (Optional)
Cumene Distillation Column
Distilled Cumene Receiver Tank(s)
Cumene Bottoms Receiver Tank
Nitrogen (Or Methane) For Pad
Bulk Cumene Storage Tanks
Finished Cumene To Sales Or In-Plant Use
Cumene Bottoms
Return To Refinery For Use In Gasoline Pool Or As Fuel.
1
2
3
4
5
6
7
8
9
10
11
12
A1
A2
A3
K
K2A
K2B
K2C
K4
K5
K6
C

Fig. III-1. Flow Diagram for Uncontrolled Model Plant Producing Cumene by Use of Solid Phosphoric Acid Catalyst

the residual hydrocarbon stream (K_3) (principally propane) can then be returned to the refinery for use as feedstock or fuel gas. Higher boiling olefins such as butylene should be removed from the propylene stream before they are used to manufacture cumene.

The benzene (stream 4) used in this process does not have to be dried before it is used, since the catalyst system requires small amounts of water vapor in the reactor stream to activate the catalyst. The feed ratio is normally at least 4 moles of benzene (stream 4) per mole of propylene (stream 1).[4]

Product purification is relatively simple with this catalyst, since no catalyst removal processing is required. The propane (streams 9 and K_3), the recycle benzene (stream 3), and the cumene product (stream 12) can each be separated by distillation. The residual bottoms (stream K_6) from the cumene distillation column can be returned to the refinery for reforming or be used in the "gasoline pool" or burned as fuel by inclusion in a fuel gas system.

The main process vent (A_1) is associated with the depropanizer column and its overhead receiver. Methane (or nitrogen) is used to blanket this system. A pressure-control valve relieves excess pressure on this system by bleeding off to the fuel gas system a mixture of methane (or nitrogen), propane, and accumulated inert gases that are carried into the process with the crude propylene (stream 1).

The second process vent (A_2) is associated with the benzene recovery column. This column is normally operated under pressure and is padded with methane (or nitrogen). As pressure and receiver levels fluctuate, a pressure-control valve relieves excess pressure on this system by bleeding off to the fuel gas system a mixture of methane (or nitrogen), benzene vapor, and residual inert gases.

The third process vent (A_3) is associated with the cumene distillation column. This column is normally operated slightly above atmospheric pressure and is padded with methane (or nitrogen) to protect the cumene from contact with the air. As pressure and receiver levels fluctuate, a pressure-control valve relieves excess pressure on this system by bleeding off a mixture of methane (or nitrogen) and cumene vapor.

Solid wastes (streams K_1 and K_5 respectively) are produced from the packed-bed reactor and from the optional clay treatment vessels. These two solids streams are not large, since they result from the periodic discharge of exhausted or depleted bed solids, but the solids can contain some volatile organic compounds (VOC). Purging and/or steam cleaning of the solids beds before the exhausted solids are discharged would minimize the residual VOC they contain.

Contaminated wastewater streams (K_{2A}, K_{2B}, and K_{2C} respectively) exit from the depropanizer column, the propane receiver tank, and the benzene receiver tank. These wastewater streams will contain small quantities of dissolved VOC. The principal contaminates will be benzene in streams K_{2A} and K_{2C} and propane in stream K_{2B}. The wastewater stream (principally K_{2A}) will also contain dissolved phosphoric acid and small quantities of dissolved or emulsified alkylbenzenes such as cumene and diisopropylbenzene.

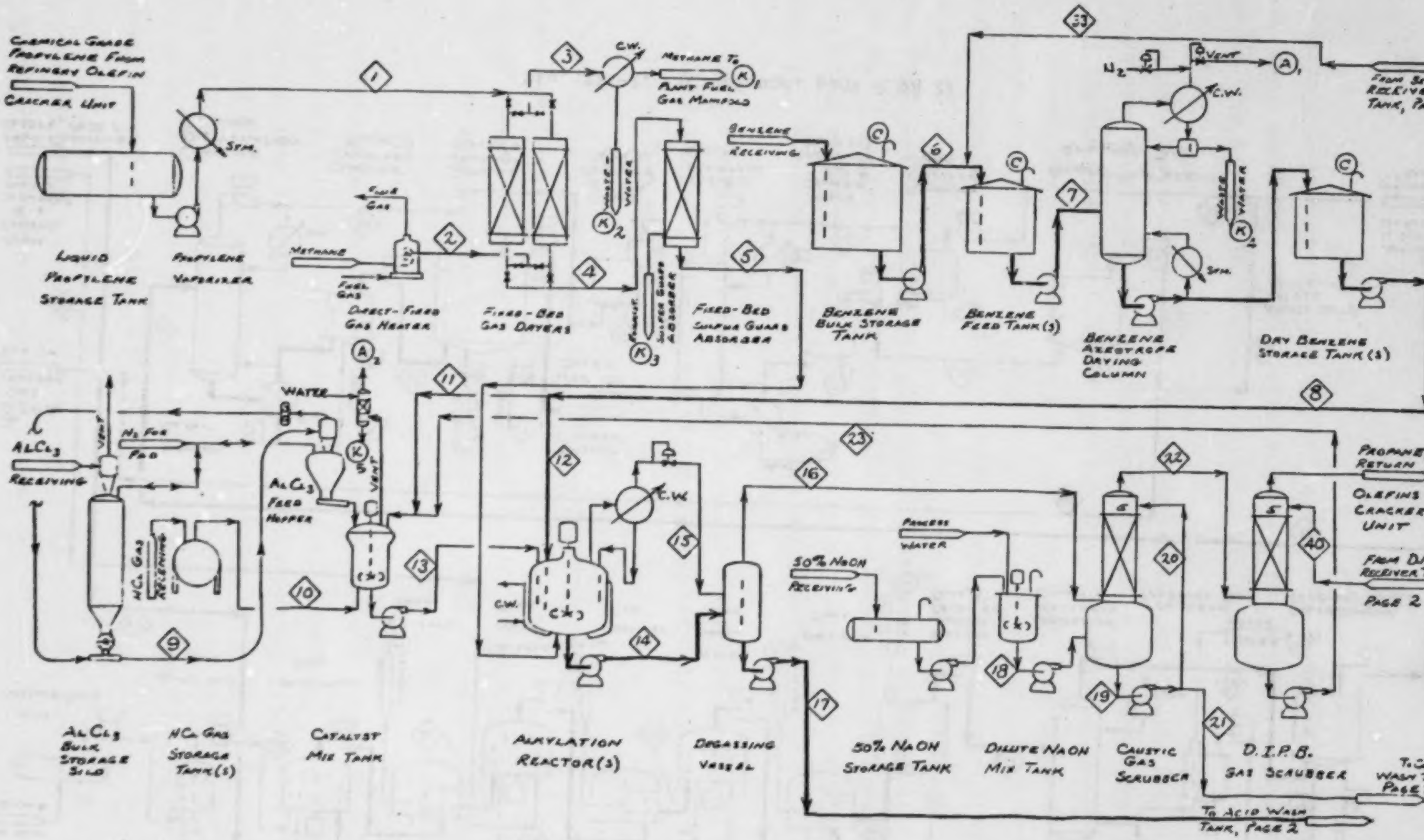
Propane is extracted from the crude product (stream 6) by the depropanizer column. Some of the extracted propane is recycled (stream 9) to the reactor for cooling, with the balance (stream K_3) returned to the refinery for reuse.

The bottoms (stream K_6) from the cumene distillation column contain principally diisopropylbenzene, along with small amounts of other high-boiling materials. This stream is returned to the refinery for reforming, for use in the refinery gasoline pool, or for use as fuel. The overhead (stream 12) from this column is the cumene product.

A purge stream (K_4) of benzene is taken as a side stream from the recycle benzene (stream 3) extracted from the crude product (stream 10) by the benzene recovery column. The purge stream, which is sent back to the refinery for purification, reforming, or use in the refinery gasoline pool, contains the small amount of ethylbenzene and similar low boilers that were generated in the alkylation of benzene with the crude propylene feed.

2. Aluminum Chloride Catalyst[5]

Figure III-2, pp. 1 and 2, is a typical flowsheet for cumene manufacture using aluminum chloride as the alkylation catalyst. Aluminum chloride is a much more active and much less selective alkylation catalyst than solid phosphoric acid. Since aluminum chloride also functions as a transalkylation catalyst, diisopropyl-


CHEMICAL GRADE PROPYLENE FROM REFINERY OLEFIN CRACKER UNIT
STM.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
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16
17
18
19
20
21
22
23
33
40
C.W.
METHANE TO PLANT FUEL GAS MANIFOLD
K1
K2
K3
K4
K5
K6
FLUE GAS
METHANE
FUEL GAS
WASTE WATER
PURGE
SULFER GUARD ABSORBER
BENZENE RECEIVING
C
N2
VENT
A1
A2
FROM BENZENE RECEIVER TANK, PAGE 2
LIQUID PROPYLENE STORAGE TANK
PROPYLENE VAPORIZER
DIRECT-FIRED GAS HEATER
FIXED-BED GAS DRYERS
FIXED-BED SULFUR GUARD ABSORBER
BENZENE BULK STORAGE TANK
BENZENE FEED TANK(S)
BENZENE AZEOTROPE DRYING COLUMN
DRY BENZENE STORAGE TANK(S)
WATER
AlCl3 RECEIVING
N2 FOR PAD
VENT
HCl GAS RECEIVING
AlCl3 FEED HOPPER
(*)
(k)
C.W.
50% NaOH RECEIVING
PROCESS WATER
PROPANE, RETURN TO OLEFINS CRACKER UNIT
FROM D.I.P.B. RECEIVER TANK PAGE 2
AlCl3 BULK STORAGE SILO
HCl GAS STORAGE TANK(S)
CATALYST MIX TANK
ALKYLATION REACTOR(S)
DEGASSING VESSEL
50% NaOH STORAGE TANK
DILUTE NaOH MIX TANK
CAUSTIC GAS SCRUBBER
D.I.P.B. GAS SCRUBBER
TO CAUSTIC WASH TANK PAGE 2
TO ACID WASH TANK, PAGE 2

Fig. III-2. Flow Diagram for Uncontrolled Model Plant Producing Cumene by Use of Aluminum Chloride Catalyst

(Page 1 of 2)

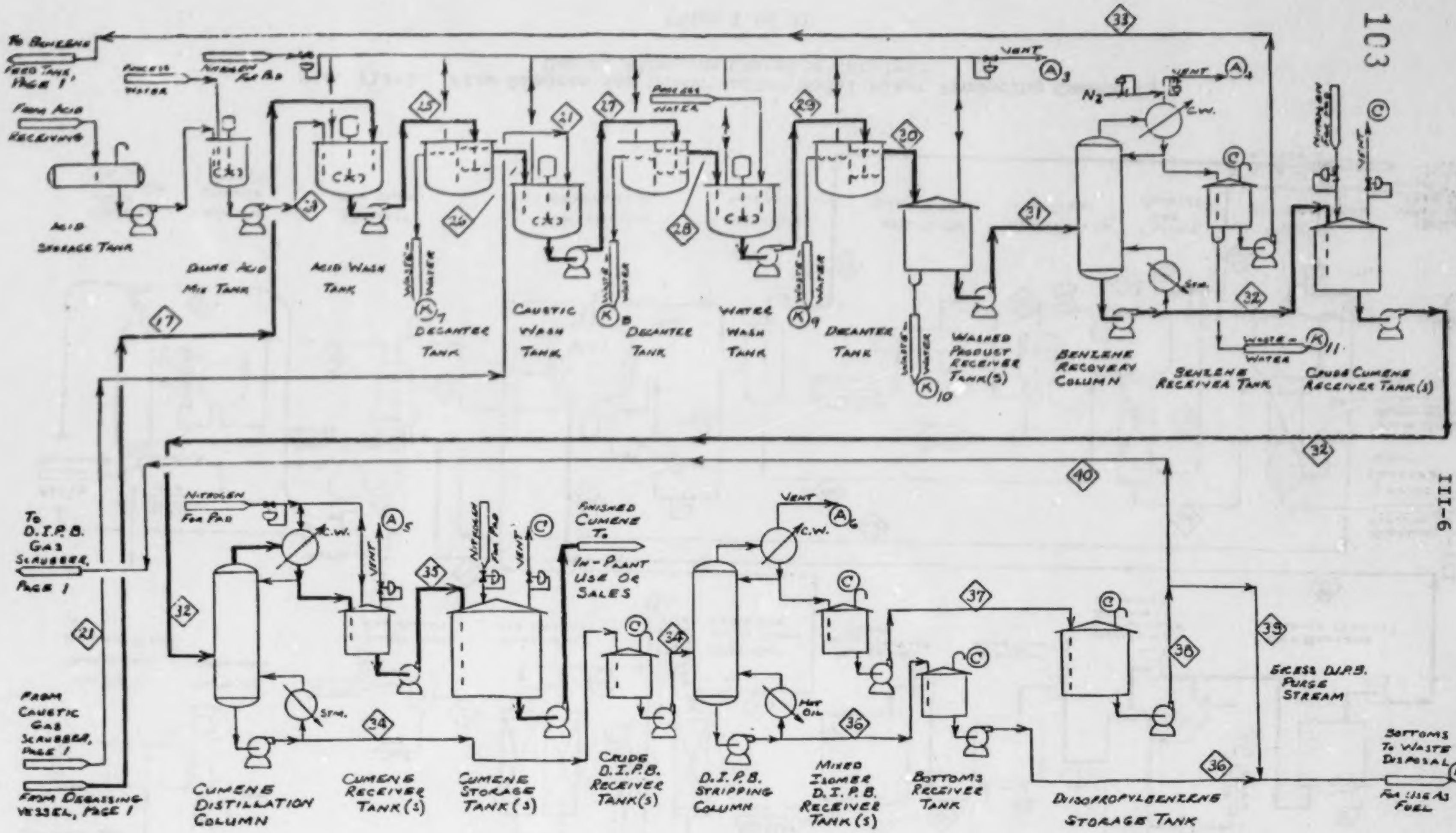
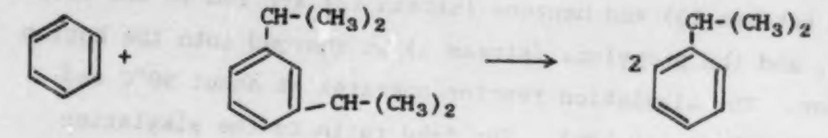

To Benzene Feed Tank, Page 1
From Acid Receiving
Acid Storage Tank
Process Water
Nitrogen For Pad
Dilute Acid Mix Tank
Acid Wash Tank
Decanter Tank
Caustic Wash Tank
Decanter Tank
Water Wash Tank
Decanter Tank
Washed Product Receiver Tank(s)
Benzene Recovery Column
Benzene Receiver Tank
Crude Cumene Receiver Tank(s)
Process Water
Waste Water
Vent
N2
C.W.
Stm.
A3
A4
K7
K8
K9
K10
K11
17
19
25
26
21
27
28
29
30
31
32
33
To D.I.P.B. Gas Scrubber, Page 1
From Caustic Gas Scrubber, Page 1
From Degassing Vessel, Page 1
21
Nitrogen For Pad
Cumene Distillation Column
Cumene Receiver Tank(s)
Cumene Storage Tank(s)
Finished Cumene To In-Plant Use Or Sales
Crude D.I.P.B. Receiver Tank(s)
D.I.P.B. Stripping Column
Mixed Isomer D.I.P.B. Receiver Tank(s)
Bottoms Receiver Tank
Diisopropylbenzene Storage Tank
Excess D.I.P.B. Purge Stream
Bottoms To Waste Disposal
For Use As Fuel
Vent
C.W.
Stm.
Hot Oil
A5
A6
C
K
32
34
35
36
37
38
39
40

Fig. III-2. (Continued, page 2 of 2)

benzene can be recycled back to the reaction system, where it reacts with excess benzene to produce additional cumene. A simple equation for this transalkylation reaction is as follows:



(benzene) (mixed isomers of D.I.P.B.) (cumene)

To prevent the generation of undesirable contaminating by-products, the propylene used with this catalyst system must be purified to at least chemical grade (95%+ purity) and must contain no more than minute amounts of other olefins such as ethylene and butylene. This propylene feedstock (stream 1) must also be dried (stream 4) and treated to remove any residual organic sulfur compounds (stream 5).

Treatment of the propylene to remove residual water in fixed-bed dryers and regeneration of the bed with heated methane generate a contaminated methane (stream K_1) that can be fed to the plant fuel gas manifold. The wastewater (stream K_2) generated by this process will contain traces of dissolved methane and VOC.

Treatment of the propylene in a sulfur guard absorber will generate waste solid (stream K_3) in the form of spent absorbent. This waste solid will contain only minor traces of VOC as propylene.

The benzene used in this process must be azeotropically dried (stream 7) to remove dissolved water. The wastewater (stream K_4) generated by the drying step is saturated with dissolved benzene at about 2000 g/Mg of water. The azeotrope drying distillation generates a vent gas (stream A_1) that is rich in benzene.

The aluminum chloride used as a catalyst in this process is received and handled as a dry powder (stream 9). Benzene (stream 11) and diisopropylbenzene (stream 23) are fed to a catalyst mix tank, where the aluminum chloride powder is added to form the catalyst complex. This mixture is treated with hydrogen chloride gas (stream 10) to activate the catalyst complex. The catalyst preparation operation generates a vent gas consisting of inert gases and hydrogen chloride gas saturated with vapors of benzene and diisopropylbenzene. The scrubber is used to absorb HCl gas, and the residual vapors (stream A_2) are then vented.

The catalyst suspension (stream 13) and benzene (stream 12) are fed to the alkylation reactor as liquids, and the propylene (stream 5) is sparged into the bottom of the reactor as a vapor. The alkylation reactor operates at about 90°C and at relatively low pressure (about 150 kPa). The feed ratio to the alkylation reactor is maintained at or above 4 moles of benzene per mole of propylene to minimize formation of polyalkylated products and to permit transalkylation of the recycle diisopropylbenzene to cumene. Since the alkylation reaction is exothermic, heat is removed by jacket cooling water and/or by use of a reflux condenser. A control valve after the reflux condenser maintains pressure in the reactor system by discharging accumulated propane (stream 15) to the degassing vessel as the reactor pressure rises above the setpoint.

The crude reaction mixture (stream 14) from the alkylation reactor is sent to the degassing vessel, where dissolved low-boiling hydrocarbons (such as propane) are released from solution.

The hydrocarbon vapor (stream 16) from the degassing vessel is sent to the caustic gas scrubber, where a weak caustic solution (stream 18) is injected into the scrubber system. The caustic solution (stream 20) is recycled over the scrubber packing for absorption of residual hydrogen chloride out of the gas stream. A side stream (21) of caustic solution is sent to the caustic wash tank.

The caustic washed hydrocarbon vapor (stream 22) is sent to the D.I.P.B. gas scrubber, where it is contacted by recycled D.I.P.B. (stream 40). The D.I.P.B. scrubber is used to extract residual unreacted propylene from the nonreactive propane in the gas. After the vapor is scrubbed, the waste gas (stream K_6) is returned to the refinery, where it either is recycled to the olefins cracker unit or is used as fuel gas. The D.I.P.B. liquid (stream 23) that contains the absorbed propylene is sent to the catalyst mix tank.

The degassed product (stream 17) is sent to the acid wash tank, where it is contacted with a weak acid solution (stream 24), which breaks down the catalyst complex and dissolves the aluminum chloride in the water layer. The hydrocarbon portion of the catalyst complex blends with the rest of the hydrocarbon layer. The water-hydrocarbon mixture (stream 25) is sent to the first decanter tank for separation of the two layers. The wastewater (stream K_7) from this decanter tank contains some weak acid, dissolved aluminum chloride, and dissolved and suspended residual hydrocarbons (principally benzene) as contained VOC.

The hydrocarbon layer (stream 26) from the first decanter tank enters the caustic wash tank, where it is mixed with the dilute caustic (stream 21) from the caustic gas scrubber. This dilute caustic layer extracts and neutralizes any residual acid carried by the hydrocarbon layer. The mixed layers (stream 27) are sent to the second decanter tank, where the hydrocarbon and aqueous layers settle and separate. The wastewater (stream K_8) from the second decanter tank contains salt, traces of residual caustic, and some dissolved or suspended hydrocarbons (principally benzene) as contained VOC.

The hydrocarbon layer (stream 28) from the second decanter tank enters the water wash tank, where it is mixed with fresh process water. This fresh process water extracts and removes any residual salt or other water soluble material from the hydrocarbon layer. The mixed layers (stream 29) from the water wash tank are sent to the third decanter tank, where the hydrocarbon and aqueous layers settle and separate. The wastewater (stream K_9) from the third decanter tank contains traces of salt and some dissolved or suspended hydrocarbons (principally benzene) as contained VOC.

The decanted hydrocarbon layer (stream 30) is stored in a washed-product receiver tank. Traces of residual suspended water settle out in this receiver tank, and the residual wastewater (stream K_{10}) is periodically drained from the collection sump of the receiver tank. This wastewater contains traces of salt and some dissolved or suspended hydrocarbons (principally benzene) as contained VOC.

The entire wash-decanter system is tied together by one common vent-pad line that furnishes nitrogen for blanketing this series of tanks. A pressure control valve on the end of the vent-pad manifold periodically releases vent gas (stream A_3) as levels rise and fall in the various tanks of the wash-decanter system. The vent gas is saturated with water vapor and hydrocarbon vapor (principally benzene) as contained VOC.

The crude product (stream 31) from the washed-product receiver tank is sent to the benzene recovery column, where the excess benzene is stripped out of the crude product. The recovered benzene (stream 33) is returned to the benzene feed tank, and the crude cumene (stream 32) is stored in the crude cumene receiver tank. Some residual water (stream K_{11}) accumulates in the benzene-receiver-tank collection sump and is periodically drained. This wastewater contains some dissolved and/or suspended benzene as contained VOC. The vent line associated with the benzene recovery column and with the benzene receiver tank releases some vent gas (stream A_4). This vent gas is principally inert gas saturated with benzene vapor as the contained VOC.

The crude cumene (stream 32) is sent to the cumene distillation column for distillation of the cumene product (stream 35). The cumene distillation column and the associated cumene receiver tank are operated above atmospheric pressure and are blanketed with nitrogen (or methane) to protect the cumene from reaction with oxygen from the air to form cumene hydroperoxide. The vent line associated with the cumene distillation column and with the cumene receiver tank releases some vent gas (stream A_5). This vent gas is nitrogen (or methane) saturated with cumene vapor as the contained VOC.

The crude D.I.P.B. (stream 34) is the bottoms stream from the cumene distillation column. This bottoms stream contains a small amount of cumene, along with mixed isomers of diisopropylbenzene (D.I.P.B.) and a small amount of higher boiling alkylbenzenes and miscellaneous tars. The crude D.I.P.B. stream is sent to the D.I.P.B. stripping column, where it is stripped away from the residual higher boiling alkylbenzenes and tars. This stripping column is normally operated under vacuum because of the high boiling points of the D.I.P.B. isomers (about 200 to 210°C at atmospheric pressure). The vacuum system on the stripping column does draw a vent stream (stream A_6) from the column condenser, and this vent stream is air (or inert gas) saturated with cumene and D.I.P.B. vapors as the contained VOC. Depending on the design and operation of the vacuum system for the column, part or all of the vent gas (stream A_6) could be discharged to the atmosphere. The portion of the VOC in stream A_6 that is not discharged directly to the atmosphere would probably end up as a secondary waste stream that could either be recovered for recycle or be sent to a waste disposal facility.

The distilled D.I.P.B. (stream 37) from the D.I.P.B. stripping column is recovered and stored in the diisopropylbenzene storage tank.

The bottoms (stream 36) from the D.I.P.B. stripping column are stored in a bottoms receiver tank and then sent to waste disposal for use as a fuel.

If excess distilled D.I.P.B. is accumulated from the cumene manufacturing (alkylation) process, it (stream 39) can be added to the bottoms (stream 36) and the combined waste stream (K_{11}) be sent to waste disposal.

The recycle D.I.P.B. (stream 40) is sent to the D.I.P.B. gas scrubber, where it is used to absorb residual propylene from the propane waste gas stream. This recycle D.I.P.B. eventually returns to the alkylation reactor, where it is transalkylated with excess benzene to generate additional cumene.

3. Other Catalysts

Other alkylation catalysts, such as concentrated sulfuric acid or anhydrous hydrogen fluoride, can be used to catalyze the alkylation of benzene with propylene to form cumene, but it is not known whether any of the present commercial producers of cumene use any of these alternative catalysts. All the manufacturers of cumene on which information on catalysts is known use either a solid phosphoric acid catalyst or an aluminum chloride complex. If an alternate catalyst such as concentrated sulfuric acid is used, the process and its characteristic emissions would be similar to the process described for the aluminum chloride catalyst system.

C. REFERENCES*

1. T. C. Gunn, "CEH Product Review on Cumene," pp. 638.5030A—N in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (March 1977).

2. Y. C. Yen, Phenol, Supplement A, pp. 19—41, Report No. 22A, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (Sept. 1972).

3. D. J. Ward, "Cumene," pp. 543—546 in Kirk-Othmer Encyclopedia of Chemical Technology, 2d ed., Vol. 6, edited by A. Standen *et al*., Wiley, New York, 1967.

4. R. H. Rosenwald, "Alkylation," pp. 58—61 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., Vol. 2, edited by M. Grayson *et al*., Wiley-Interscience, New York, 1978.

5. F. D. Bess, letter dated Sept. 21, 1978, to EPA from Union Carbide Corp., South Charleston, WV, in response to EPA's request for information on the cumene process.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Sections 111 and 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to oxone formation. It should be noted that although ethane is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. SOLID PHOSPHORIC ACID CATALYST PROCESS

1. Model Plant[1—6]

The model plant* for this study on the solid phosphoric acid catalyst process for the manufacture of cumene has a production capacity of 227 Gg/yr based on 8760 hr/yr.** Actual capacities of the newer production plants using this catalyst system vary from 181.4 to 317.5 Gg/yr. The flow diagram of the model plant shown in Fig. III-1 is typical of today's manufacturing and engineering technology. The process shown is not necessarily identical to that used by any of the actual operating plants, but the technology represented is close enough to be suitable for emission control studies. Characteristics of the model plant important to air dispersion are shown in Table B-1, Appendix B.

2. Sources and Emissions

Sources and emission rates for the solid phosphoric acid catalyst process are summarized in Table IV-1.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Table IV-1. Total Uncontrolled[a] VOC Emissions from the Model Plant for the Cumene Manufacturing Process Using Solid Phosphoric Acid Catalyst (227 Gg/yr)

Emission Source	Stream Designation (Fig. III-1)	VOC Emissions[b]		Vent Gas VOC Emission Composition (wt %)						Non-VOC in Vent Gas (wt %)
		Ratio (g/kg)[c]	Rate (kg/hr)	C_2	C_3	C_4	Higher Aliphatics	Benzene	Alkylbenzenes	
Cumene distillation system vent	A_3	0.03	0.9	11.7[d]	3.9[d]	6.1[d]	0	Trace	78.3	64.1
Fugitive		0.24	6.32							
Storage and handling		0.27	7.11							
Secondary		0.008	0.2							
Total		0.55	14.5							

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[a] Uncontrolled emissions are emissions from the process for which no specific emission control devices (other than those necessary for economical operation) have been installed.

[b] VOC emissions exclude methane, but include higher molecular weight organic compounds such as ethane, ethylene, propane, propylene, butane, butenes, benzene, and various alkylbenzenes.

[c] g of emissions per kg of cumene produced.

[d] The C_2, C_3, and C_4 indicated here are brought into the system with the crude methane used as an inert-gas blanket. If pure methane or nitrogen were used as an inert-gas blanket, these emissions would not be present.

a. Cumene Distillation System Vent[1—6]——The cumene distillation system operates slightly above atmospheric pressure to ensure that no air contacts the cumene product. Cumene oxidizes easily to cumene hydroperoxide when contacted with oxygen from the air, and the presence of cumene hydroperoxide (especially in a cumene distillation system) could be very hazardous, since the vapor pressure of cumene hydroperoxide is much lower (higher boiling point) than that of cumene and could cause the cumene hydroperoxide to decompose violently if it accumulates in the reboiler of the cumene distillation system.

The distillation system is pressurized with crude methane to maintain a minimum pressure. As the pressure in the system fluctuates, a vent stream of crude methane saturated with cumene vapors is periodically released through the pressure control valve. The amount and composition given in Table IV-1 are intended to represent typical emissions from a well-designed and -operated plant. If nitrogen is used instead of crude methane for pressurization, the VOC emissions will be less because the VOC from the crude methane will not be present. The VOC emissions will be approximately the same as those shown for the model plant for the aluminum chloride catalyst process (see Sect. IV-B-e) when nitrogen is used.

The crude methane stream is used to initially pressurize the cumene distillation system and to maintain a minimum pressure on the system during operating. The methane charged to the system is eventually vented (A_3, Fig. III-1) along with other hydrocarbon vapors. The crude methane is also used to purge the system of liquid hydrocarbons during shutdowns and to drive out oxygen-containing air before startups.

b. Fugitive Emissions——Process pumps, piping flanges, and valves are potential sources of fugitive emissions. The model plant is estimated to have 28 pumps in light-liquid service, 200 process valves in light-liquid service, and 6 control valves (safety-relief valves) in vapor service. The factors in Appendix C were used to determine the emission contribution of these equipment components. For the model plant it is estimated that approximately 6.32 kg/hr as VOC is lost to the atmosphere.

c. Storage and Handling Emissions[7,8]——Emissions result from the storage and handling of raw materials, intermediates, and finished products. A list of the storage tanks, the materials stored, and the assumed turnovers per year for the model plant is given in Table IV-2. For material that is not produced or consumed captively it is assumed that shipment is by rail car or by barge. The uncontrolled emissions were calculated based on fixed-roof tanks, painted white, with conservation vents. Day-night temperature variations were assumed to average 11.1°C. Emission equations from AP-42 were used with one modification. The breathing losses were divided by 4 to account for recent evidence that the AP-42 breathing-loss equation overpredicts emissions.

d. Secondary Emissions[1—6]—The principal sources of secondary VOC emissions are the process wastewater streams from the depropanizer column, the propane receiver tank, and the benzene receiver tank. It is assumed that these wastewater streams are combined and sent through an oil skimmer tank for removal of any floating layer of hydrocarbons and that the oily skimmings are returned to the process. After the skimming step, it is assumed that the combined process wastewater stream is sent to the plant wastewater system. This wastewater will still contain dissolved hydrocarbons, such as propane (trace), benzene (up to 2000 ppm of water), and assorted alkylbenzenes (up to 400 ppm of water). The total wastewater flow is estimated to be 75 kg/hr for the model plant. The amount of benzene and alkylbenzene in the wastewater is estimated to be approximately 0.2 kg/hr.

Extremely minor sources of secondary VOC emissions are the waste catalyst from the multistage packed-bed reactor and the spent clay from the optional clay treatment vessels. No estimate of the amount of VOC from these solid-waste sources has been made.

B. ALUMINUM CHLORIDE CATALYST PROCESS

1. Model Plant[1,9]

The model plant for this study on the aluminum chloride catalyst process for the manufacture of cumene has a production capacity of 227 Gg/yr based on 8760 hr/yr. The actual capacity of the one known cumene plant using an aluminum chloride catalyst is 290 Gg/yr. There may be other plants (in the unknown-catalyst category) that also use this catalyst system for the manufacture of cumene. The flow diagram of the model plant shown in Fig. III-2 is typical of today's manufacturing and engineering technology. The process is not necessarily identical

Table IV-2. Storage Tank Data for Model Plant Producing Cumene by Process Using Solid Phosphoric Acid Catalyst

Contents	Tank Size (m^3)*	Turnovers per Year	Bulk Temperature (°C)	Losses (kg/hr)
Benzene	8891	20	20	6.08
Cumene bottoms	334	77	20	0.009
Finished cumene	870	150	20	0.111
Finished cumene	870	150	20	0.111
Cumene	8891	14.8	20	0.399
Cumene	8891	14.8	20	0.399
Total				7.11

*Fixed-roof tanks, painted white, with conservation vents; day-night temperature variation averages 11.1°C.

to that used by any actual operating plant, but the technology represented is close enough to be suitable for emission control studies. Characteristics of the model plant important to air dispersion are shown in Table B-2, Appendix B.

2. Sources and Emissions

Sources and emission rates for the aluminum chloride catalyst process are summarized in Table IV-3.

a. Benzene Azeotrope Drying Column Vent[1,9]——The vent (A_1, Fig. III-2) from the benzene azeotrope drying system discharges inert gas, water vapor, and benzene vapor. This azeotrope distillation system operates above atmospheric pressure and is blanketed by nitrogen (inert gas) to maintain column pressure and to purge the column during shutdowns and startups. A pressure control valve is used to maintain column pressure, and the discharge from this control valve contains the VOC that is released. The composition and amount of this stream are controlled by the vapor pressure of the benzene-water condensate and by the amount of inert gas that must be vented. The amount and composition given in Table IV-3 are intended to represent typical emissions from a well-designed and operated process.

b. Catalyst Mix Tank Scrubber Vent[1,9]——The vent (A_2, Fig. III-2) from the catalyst mix tank discharges a mixture of HCl gas and organic vapor consisting principally of benzene and some diisopropylbenzene. Since HCl gas is both toxic and corrosive, this vent gas cannot be released directly to the atmosphere without treatment. Normal treatment consists of scrubbing with water or an alkaline solution to absorb and remove the HCl gas. Most of the organic vapors will also be condensed and dissolved by the scrubber water used to remove the HCl. The residual vent gas discharged by the scrubber will also carry some residual organic vapors with it. The amount and composition given in Table IV-3 are intended to represent typical emissions from the vent of the scrubber in a well-designed and operated process.

c. Wash-Decanter System Vent[1,9]——The vent (A_3, Fig. III-2, p. 2) from the wash-decant system is shown as a common header with a nitrogen pad and a single relief-valve outlet. Since the wash-decant system operates continuously with no significant changes in liquid levels, the normal discharge from this vent is zero. Level

Table IV-3. Total Uncontrolled[a] VOC Emissions from Model Plant for the Cumene Manufacturing Process Using Aluminum Chloride Catalyst (227 Gg/yr)

Emission Source	Stream Designation (Fig.III-2)	VOC Emissions[b] Ratio (g/kg)[c]	VOC Emissions[b] Rate (kg/hr)	Vent Gas VOC Emission Composition (wt %) C_3	Vent Gas VOC Emission Composition (wt %) Benzene	Vent Gas VOC Emission Composition (wt %) Alkylbenzene	Non-VOC in Vent Gas (wt %)
Benzene azeotrope drying column	A_1	0.02	0.54		100		72
Catalyst mix tank scrubber	A_2	0.16	4.0	Trace	99.4	0.6	66
Wash-decanter system	A_3	0.01	0.3		78.4	21.6	68
Benzene recovery column	A_4	0.017	0.43		100		72
Cumene distillation system	A_5	0.003	0.07			100	79
D.I.P.B. stripping system	A_6	0.0009	0.02			100	91
Fugitive		0.51	13.3				
Storage and handling		0.97	25.1				
Secondary		0.23	6.0				
Total		1.92	49.8				

[a] Uncontrolled emissions are emissions from the process for which no specific emission control devices (other than those necessary for economic or safety reasons) have been installed.

[b] VOC emissions exclude methane, but include higher molecular weight organic compounds such as ethane, ethylene, propane, propylene, butane, butenes, benzene, and various alkylbenzenes.

[c] g of emissions per kg of cumene produced.

fluctuations during startups and shutdowns can cause intermittent venting of nitrogen gas contaminated with organic vapors, such as benzene, cumene, etc. The amount and composition given in Table IV-3 are intended to represent the average emissions generated by the periodic releases from this wash-decant system in a well-designed and operated process.

d. Benzene Recovery Column Vent[1,9]——The vent (A_4, Fig. III-2, p. 2) from the benzene recovery column discharges inert gas, water vapor, and benzene vapor. This benzene recovery column operates above atmospheric pressure and is blanketed with nitrogen (inert gas) to maintain column pressure and to purge the column during startups and shutdowns. A pressure control valve is used to maintain column pressure, and discharges from this control valve contain the VOC that is released. The composition and amount of VOC in this stream are controlled by the vapor pressure of the benzene-water condensate and the amount of inert gas that must be vented. The amount and composition given in Table IV-3 are intended to represent typical emissions from a well-designed and operated process.

e. Cumene Distillation System Vent[1,9]——The vent (A_5, Fig. III-2, p. 2) from the cumene distillation system vent contains inert gas and cumene vapor. This distillation system operates slightly above atmospheric pressure and is blanketed with nitrogen to protect the cumene from oxidation to cumene hydroperoxide by atmospheric oxygen. A pressure control valve is used to maintain column pressure, and discharges from this control valve contain the VOC that is released. The composition and amount of VOC in this stream are controlled by the vapor pressure of the cumene condensate and the amount of inert gas that must be vented. The amount and composition given in Table IV-3 are intended to represent typical emissions from a well-designed and operated process.

f. D.I.P.B. Stripping System Vent[1,9]——The vent (A_6, Fig. III-2, p. 2) from the D.I.P.B. stripping system contains inert gas (air) and diisopropylbenzene vapors. This system operates at atmospheric pressure to strip off the diisopropylbenzene from the residual high-boiling impurities. The vent gas from this system contains minor amounts of VOC in the form of diisopropylbenzene vapors. The amount of D.I.P.B. is controlled by the vapor pressure of the diisopropylbenzene condensate and the amount of inert gas that must be vented. The amount and composition given in Table IV-3 are intended to represent typical emissions from a well-designed and operated process.

g. **Fugitive Emissions**—Process pumps, piping flanges, and valves are potential sources of fugitive emissions. The model plant is estimated to have 56 pumps in light-liquid service, 500 process valves in light-liquid service, and 10 control valves (safety-relief valves) in vapor service. The factors in Appendix C were used to determine the emission contribution of these equipment components. For the model plant it is estimated that approximately 13.3 kg/hr as VOC is lost to the atmosphere.

h. **Storage and Handling Emissions**[7,8]—Emissions result from the storage and handling of raw materials, intermediates, and finished products. A list of the storage tanks, the materials stored, and the assumed turnovers per year for the model plant is given in Table IV-4. For material that is not produced or consumed captively it is assumed that shipment is by rail car or by barge. The uncontrolled emissions were calculated based on fixed-roof tanks, painted white, with conservation vents. Day-night temperature variations were assumed to average 11.1°C. Emission equations from AP-42 were used with one modification. The breathing losses were divided by 4 to account for recent evidence that the AP-42 breathing-loss equation overpredicts emissions.

i. **Secondary Emissions**[1,9]—The principal sources of secondary emissions are the various wastewater streams generated by the process. These wastewater streams are: K_2, wastewater from the gas driers; K_4, wastewater from the decanter on the benzene azeotrope drying columing; K_5, catalyst mix tank scrubber wastewater; K_7, K_8, and K_9, wastewater streams from the decanters of the product wash steps; and K_{10} and K_{11}, wastewater from the water collection sumps of the washed-product receiver tank and the benzene receiver tank. It is assumed that all these wastewater streams are collected, combined, and sent to a final oil skimmer sump for collection of any residual oil layer. After the skimming step the combined wastewater stream is sent through an underground sewer system to the plant wastewater biooxidation treatment system, and the oil layer is returned to the washed-product receiver tank. The combined wastewater stream will still contain dissolved hydrocarbons, such as benzene (up to 2000 g/mg of water) and assorted alkylbenzenes (up to 400 g/mg of water). The total wastewater flow is estimated to be about 2500 kg/hr for the model plant. This amount of benzene and alkylbenzene in the wastewater is estimated to be approximately 6 kg/hr.

Table IV-4. Storage Tank Data for Model Plant Producing Cumene by Process Using Aluminum Chloride Catalyst

Contents	Tank Size (m^3)*	Turnovers per Year	Bulk Temperature (°C)	Losses (kg/hr)
Benzene	8891	20	20	6.08
Benzene	1800	148	20	3.08
Benzene	1800	148	20	3.08
Benzene	1800	148	20	3.08
Benzene	1800	148	20	3.08
Mixture	1800	179	20	2.71
Mixture	1800	179	20	2.71
Cumene (crude)	870	165	20	0.111
Cumene (crude)	870	165	20	0.111
Cumene (finished)	870	150	20	0.111
Cumene (finished)	870	150	20	0.111
Cumene (finished)	8891	14.8	20	0.399
Cumene (finished)	8891	14.8	20	0.399
D.I.P.B. (crude)	80	161	20	0.003
D.I.P.B. (crude)	80	161	20	0.003
D.I.P.B. (finished)	80	139	20	0.001
D.I.P.B. (finished)	80	139	20	0.001
Heavy oil	17.8	101	20	0.000
D.I.P.B. (finished)	1422	16.9	20	0.009
Total				25.1

*Fixed-roof tanks, painted white, with conservation vents; day-night temperature variation averages 11.1°C.

C. OTHER PROCESSES[1]

The literature describes other catalysis schemes that will promote the alkylation of benzene with propylene to form cumene. These alternative catalyst systems include the following: phosphoric acid—boron trifloride complex; aluminum chloride—phosphoric acid complex; concentrated sulfuric acid; anhydrous hydrofluoric acid; boron-trifluoride-modified alumina; boron trifluoride complexed with either water or sulfuric acid; alkane—sulfuric acid complex; silica-alumina, with or without hydrogen chloride; zinc chloride on silica; activated clay; $VOCl_3$—$(C_2H_5)_2AlCl$; rhenium chloride; and many others. The reaction schemes using these various catalysts would be similar to that for either the solid phosphoric acid catalyst process or the aluminum chloride catalyst process, and their characteristic emissions would also be similar. Although other catalyst systems have been described and patented, the two systems (solid phosphoric acid and aluminum chloride) seem to dominate the industry, with the solid phosphoric acid route being preferred by most producers.

D. REFERENCES*

1. Y. C. Yen, Phenol, Supplement A, pp. 19—41, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (September 1972).

2. J. R. Kampfhenkel, letter dated Sept. 12, 1978, to EPA from Sun Petroleum Products Co., Corpus Christi, TX, in response to EPA's request for information on the cumene process.

3. M. P. Zanotti, letter dated Sept. 19, 1978, to EPA from Gulf Oil Co., Port Arthur, TX, in response to EPA's request for information the cumene process.

4. Oliver J. Zandona, letter dated Sept. 25, 1978, to EPA from Ashland Petroleum Co., Ashland, KY, in response to EPA's request for information on the cumene process.

5. Michael A. Pierle, letter dated Oct. 23, 1978, to EPA from Monsanto Chemical Co., St. Louis, MO, in response to EPA's request for information on the cumene process.

6. Attachment II, Information on the Cumene Process, from Shell Oil Co., Deer Park, TX, in response to EPA's request for information on the cumene process.

7. C. C. Masser, "Storage of Petroleum Liquids," Sect. 4.3 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

8. E. C. Pulaski, TRW, letter dated May 30, 1979, to Richard Burr, EPA.

9. F. D. Bess, letter dated Sept. 21, 1978, to EPA from Union Carbide Corp., South Charleston, WV, in response to EPA's request for information on the cumene process.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. SOLID PHOSPHORIC ACID CATALYST PROCESS[1—5]

1. Cumene Distillation System Vent

The stream from the cumene distillation system vent (A_3, Fig. III-1) consists principally of cumene vapors, together with some low-molecular-weight C_2, C_3, and C_4 hydrocarbons that are introduced with the crude methane used to blanket the distillation system. Heating value of this vent stream (including the methane used for blanketing) is approximately 0.13 GJ/hr for the model plant.

The control system evaluated for this vent stream is the installation of a piping manifold to direct the vent gas, which contains VOC, to the plant emergency flare system for destruction of the VOC by thermal oxidation. A VOC removal efficiency of 95%* has been assumed when the flare is operating at less than 10% of design capacity.[6] The controlled emission for this vent is shown in Table V-1.

2. Fugitive Emission Sources

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA report.[7] Emissions from pumps and valves can be controlled by an appropriate leak-detection system, along with repair of leaky or defective equipment as needed. Controlled fugitive emissions calculated with the factors given in Appendix C are included in Table V-1. These factors are based on the assumption that major leaks are detected and corrected as noted in Appendix C.

3. Storage and Handling Sources

It is important to control the VOC emissions, particularly benzene, in the storage and handling areas because of health and safety hazards. Options for control of storage and handling emissions are covered in another EPA report.[8] For the model plant the VOC emissions from storage tanks containing benzene are controlled

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*Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies cited are for tentative comparison purposes.

Table V-1. VOC Controlled Emissions for Model Plant Producing Cumene by Process Using Solid Phosphoric Acid Catalyst[a]

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Controlled Emissions	
				Ratio (g/kg)[b]	Rate (kg/hr)
Cumene distillation system vent	A3	Plant flare	95[c]	0.0015	0.05
Fugitive		Detection and correction of major leaks	71.4	0.070	1.8
Storage and handling					
Benzene		Floating roofs	85	0.035	0.912
Other		None	0	0.040	1.029
Secondary		None	0	0.008	0.20
Total				0.155	3.99

[a] From refs 1—5.

[b] g of emissions per kg of cumene produced.

[c] 95% efficiency at less than 10% of flare design capacity.

by using floating-roof tanks* in place of fixed-roof API tanks. The controlled VOC emissions from storage tanks that contain benzene were calculated on the assumption that a contact type of internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%[9,10] and are listed in Table V-2 and summarized in Table V-1. No control has been identified for the tanks containing cumene or by-products.

4. Secondary Sources

The control of secondary emissions is discussed in a separate EPA report.[11] No control system has been identified for the model plant.

B. ALUMINUM CHLORIDE CATALYST PROCESS[12]

1. Benzene Azeotrope Drying-Column Vent

The stream from the benzene azeotrope drying-column vent (A_1, Fig. III-2) is relatively small and consists largely of benzene vapor and inert gas. The heating value of the vent vapor is approximately 0.02 GJ/hr for the model plant.

The control system evaluated for this vent stream is the installation of a piping manifold to direct the VOC-containing gas to the plant emergency flare system for destruction of the VOC by thermal oxidation. A VOC removal efficiency of 95% has been assumed when the flare is operating at less than 10% of design capacity.[6] The controlled emission for this vent is shown in Table V-3.

2. Catalyst Mix Tank Scrubber Vent

The stream from the vent (A_2, Fig. III-2) scrubber on the catalyst mix tank is the largest source of VOC process emission in the aluminum chloride catalyst cumene model plant. The VOC in this vent stream consists largely of benzene vapor. The heating value of the vent vapor is approximately 0.17 GJ/hr for the model plant.

The control system evaluated for this vent stream is the installation of a piping manifold to direct the VOC-containing gas to the plant emergency flare system for destruction of the VOC by thermal oxidation. A VOC removal efficiency of

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*Consist of internal floating covers or covered floating roofs as defined in API-2519, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

Table V-2. Storage Tank Data for Model Plant Producing Cumene by Process Using Solid Phosphoric Acid Catalyst

Contents	Tank Size (m^3)[a]	Roof Style	Turnovers per Year	Bulk Temp (°C)	Losses (kg/hr)[b]
Benzene	8891	Floating	20	20	0.912
Cumene bottoms	334	Fixed	77	20	0.009
Finished cumene	870	Fixed	150	20	0.111
Finished cumene	870	Fixed	150	20	0.111
Cumene	8891	Fixed	14.8	20	0.399
Cumene	8891	Fixed	14.8	20	0.399
Total					1.94

[a] Floating- or fixed-roof tanks painted white, with conservation vents on fixed-roof tanks; day-night temperature variation averages 11.1°C.

[b] From refs 9 and 10.

95% has been assumed when a flare is operating at less than 10% of design capacity.[6] The controlled emission for this vent is shown in Table V-3.

3. Wash-Decanter System Vent

This stream from the wash-decanter system vent (A_3, Fig. III-2, p. 2) consists principally of benzene and alkylbenzene in an inorganic gas stream. The heating value of the VOC in this vent gas is approximately 0.01 GJ/hr for the model plant.

The control system evaluated for this minor vent stream is the installation of a piping manifold to direct the VOC-containing gas to the plant emergency flare system for destruction of the VOC by thermal oxidation. A VOC removal efficiency of 95% has been assumed when the flare is operating at less than 10% of design capacity.[6] The controlled emisson for this vent is shown in Table V-3.

4. Benzene Recovery Column Vent

The stream from the benzene recovery column vent (A_4, Fig. III-2, p. 2) consists principally of benzene in an inert-gas stream and is relatively small. The heating value of the VOC in this vent gas is approximately 0.02 GJ/hr for the model plant.

The control system evaluated for this vent stream is the installation of a piping manifold to direct the VOC-containing gas to the plant emergency flare system for destruction of the VOC by thermal oxidation. A VOC removal efficiency of 95% has been assumed when the flare is operating at less than 10% of design capacity.[6] The controlled emission for this vent is shown in Table V-3.

5. Cumene Distillation System Vent

The stream from the cumene distillation system vent (A_5, Fig. III-2, p. 2) consists principally of cumene in an inert-gas stream. This vent stream contains a very small amount of VOC, whose heating value is approximately 3 MJ/hr.

Since this VOC emission is so low, no emission control system was evaluated. The emission from this vent is shown in Table V-3.

Table V-3. VOC Controlled Emissions for Model Plant Producing Cumene by Process Using Aluminum Chloride Catalyst[a]

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Controlled Emissions	
				Ratio (g/kg)[b]	Rate (kg/hr)
Benzene azeotrope drying column	A1	Plant flare	95	0.001	0.027
Catalyst mix tank scrubber	A_2	Plant flare	95	0.008	0.20
Wash-decanter system	A_3	Plant flare	95	0.0005	0.015
Benzene recovery column	A_4	Plant flare	95	0.00085	0.022
Cumene distillation system	A_5	None	0	0.003	0.07
D.I.P.B. stripping system	A_6	None	0	0.0009	0.02
Fugitive		Detection and correction of major leaks	71.5	0.146	3.79
Storage and handling					
Benzene		Floating roofs	85	0.138	3.57
Other		None	0	0.049	1.26
Secondary		None	0	0.23	6.0
Total				0.577	15.0

[a] From ref 12.

[b] g of emissions per kg of cumene produced.

6. **D.I.P.B Stripping System Vent**

This stream from the D.I.P.B. stripping system vent (A_6, Fig. III-2, p. 2) consists principally of D.I.P.B. vapors in an inert-gas stream. This vent stream contains an extremely small amount of VOC, which has a heating value of approximately 0.8 MJ/hr.

Since this VOC emission is so low, no emission control system was evaluated. The emission from this vent is shown in Table V-3.

7. **Fugitive Emission Sources**

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA report.[7] Emissions from pumps and valves can be controlled by an appropriate leak-detection system, along with repair of leaky or defective equipment as needed. Controlled fugitive emissions calculated with factors given in Appendix C are included in Table V-3. These factors are based on the assumption that major leaks are detected and corrected as described in Appendix C.

8. **Storage and Handling Sources**

It is important to control the VOC emissions, particularly benzene, in the storage and handling areas because of health and safety hazards. Options for control of storage and handling emissions are covered in another EPA report.[8] For the model plant the VOC emissions from storage tanks containing benzene are controlled by using floating-roof tanks in place of fixed-roof API tanks. The controlled VOC emissions from storage tanks that contain benzene were calculated on the assumption that a contact type of internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%[9,10] and are listed in Table V-4 and summarized in Table V-3. No controls have been identified for tanks containing cumene or by-products.

9. **Secondary Sources**

The control of secondary emissions is discussed in a separate EPA report.[11] No control system has been identified for the model plant.

Table V-4. Storage Tank Data for Model Plant Producing Cumene by Process Using Aluminum Chloride Catalyst

Contents	Tank Size (m^3)[a]	Roof Style	Turnovers per Year	Bulk Temp (°C)	Losses (kg/hr)[b]
Benzene	8891	Floating	20	20	0.912
Benzene	1800	Floating	148	20	0.462
Benzene	1800	Floating	148	20	0.462
Benzene	1800	Floating	148	20	0.462
Benzene	1800	Floating	148	20	0.462
Mixture	1800	Floating	179	20	0.407
Mixture	1800	Floating	179	20	0.407
Cumene (crude)	870	Fixed	165	20	0.111
Cumene (crude)	870	Fixed	165	20	0.111
Cumene (finished)	870	Fixed	150	20	0.111
Cumene (finished)	870	Fixed	150	20	0.111
Cumene (finished)	8891	Fixed	14.8	20	0.399
Cumene (finished)	8891	Fixed	14.8	20	0.399
D.I.P.B. (crude)	80	Fixed	161	20	0.003
D.I.P.B. (crude)	80	Fixed	161	20	0.003
D.I.P.B. (finished)	80	Fixed	139	20	0.001
D.I.P.B. (finished)	80	Fixed	139	20	0.001
Heavy oil	17.8	Fixed	101	20	0.000
D.I.P.B. (finished)	1422	Fixed	16.9	20	0.009
Total					4.83

[a] Floating- or fixed-roof tanks, painted white, with conservation vents on fixed-roof tanks; day-night temperature variation averages 11.1°C.

[b] From refs 9 and 10.

C. OTHER PROCESSES[13]

No attempt has been made to estimate VOC emissions, sources, or possible VOC emission control techniques for other process routes or alternate catalyst systems that might be used to manufacture cumene. It is believed that the possible alternate processes and catalyst systems will be similar in equipment characteristics and process emissions to the two processes and catalyst systems described. As far as is known, only the solid phosphoric catalyst process and the aluminum chloride catalyst process are used commercially in the United States.

D. REFERENCES*

1. J. R. Kampfhenkel, letter dated Sept. 12, 1978, to EPA from Sun Petroleum Products Co., Corpus Christi, TX, in response to EPA's request for information on the cumene process.

2. M. P. Zanotti, letter dated Sept. 19, 1978, to EPA from Gulf Oil Co., Port Arthur, TX, in response to EPA's request for information the cumene process.

3. Oliver J. Zandona, letter dated Sept. 25, 1978, to EPA from Ashland Petroleum Co., Ashland, KY, in response to EPA's request for information on the cumene process.

4. Michael A. Pierle, letter dated Oct. 23, 1978, to EPA from Monsanto Chemical Co., St. Louis, MO, in response to EPA's request for information on the cumene process.

5. Attachment II, Information on the Cumene Process, from Shell Oil Co., Deer Park, TX, in response to EPA's request for information on the cumene process.

6. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

7. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

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10. W. T. Moody, TRW, Inc., letter dated Aug. 15, 1959, to D. A. Beck, EPA.

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12. F. D. Bess, letter dated Sept. 21, 1978, to EPA from Union Carbide Corp., South Charleston, WV, in response to EPA's request for information on the cumene process.

13. Y. C. Yen, Phenol, Supplement A, pp. 19—41, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (September 1972).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

Tables VI-1 and VI-2 show the environmental impacts of reducing VOC emissions from solid phosphoric catalyst cumene plants and aluminum chloride catalyst cumene plants by application of the described control systems (Sect. V) to the model plants. From an energy standpoint, typical uncontrolled model plants for both processes will consume heat in the range of 4.6 to 7.0 MJ/kg of product and will consume power in the range of 0.13 to 0.15 MJ/kg of product, while releasing about 4.8 to 7.2 MJ/kg of product to the environment in the form of low-temperature heat.[1]

1. Solid Phosphoric Acid Catalyst Process[2—6]

The emissions from the solid phosphoric acid model plant are discussed in Sect. IV, and emission control techniques are discussed in Sect. V. It is estimated that the current total domestic capacity for cumene manufacture by this process is about 1750 Gg/yr. The environmental and energy impacts for control of emissions from this process are as follows:

a. Cumene Distillation System Vent——Emissions from the cumene distillation system can be controlled by installing a piping manifold to direct the vent gas to the plant emergency flare system. In the model plant, direction of this vent gas to the plant flare would reduce VOC emissions from this source by about 7.5 Mg/yr. Burning of the VOC in the plant emergency flare system would release about 0.13 GJ/hr of heat to the environment for the model plant.

b. Fugitive Emissions——The control methods previously described for these emissions are major leak detection and correction as described in Appendix C. Application of these methods would result in a VOC emission reduction of 39.6 Mg/yr from the model plant.

c. Storage and Handling[7]——The control method previously described for reduction of VOC emissions from storage tanks consists of installing floating roofs on the tanks that handle benzene or organic mixtures containing benzene. Application of this method would reduce the VOC emissions from the model plant by about 45.3 Mg/yr.

Table VI-1. Environmental Impact of Controlled Model Plant Producing Cumene by Process Using Solid Phosphoric Acid Catalyst

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)
Cumene distillation system vent	A3	Plant flare	95	7.5
Fugitive		Detection and correction of major leaks	71.4	39.6
Storage and handling				
Benzene		Floating roofs	85	45.3
Other		None	0	0
Secondary		None	0	0
Total				92.4

Table VI-2. Environmental Impact of Controlled Model Plant Producing Cumene by Process Using Aluminum Chloride Catalyst

Emission Source	Stream Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)
Benzene azeotrope drying column vent	A_1	Plant flare	95	4.46
Catalyst mix tank scrubber vent	A_2	Plant flare	95	33.25
Wash-decanter system vent	A_3	Plant flare	95	2.52
Benzene recovery column vent	A_4	Plant flare	95	3.59
Cumene distillation system vent	A_5	None	0	0
D.I.P.B. stripping system vent	A_6	None	0	0
Fugitive		Detection and correction of major leaks	71.5	83.2
Storage and handling				
Benzene		Floating roofs	85	177
Other		None	0	0
Secondary		None	0	0
Total				304

d. 1978 Industrial Emissions—It has been estimated that the current industrial capacity for manufacture of cumene by the solid phosphoric acid catalyst process is 1750 Gg/yr. Using the figure of 57% for capacity utilization, this amounts to a production level of 1000 Gg in 1978. It has been estimated that the actual emissions from cumene manufacture by the solid phosphoric acid catalyst process were 200 Mg in 1978 (assuming current control at 85% of the level to be achieved by a controlled model plant). For the uncontrolled model plant at 227 Gg/yr the emission level is 130 Mg/yr. For the controlled model plant at 227 Gg/yr the low value for the emission level is 35 Mg/yr.

2. Aluminum Chloride Catalyst Process[8]

The emissions from the aluminum chloride catalyst process model plant are discussed in Sect. IV, and emission control techniques are discussed in Sect. V. It is estimated that the current total domestic capacity for cumene manufacture by this process or by closely allied equivalent processes is about 400 Gg/yr. The environmental and energy impacts for control of emissions from this process are as follows:

a. Benzene Azeotrope Drying-Column Vent—The control method previously described for reduction of VOC emissions from the benzene azeotrope drying column consists of installing a piping manifold to deliver this vent gas to the plant emergency flare system. Use of this method would reduce VOC emissions from the model plant by about 4.46 Mg/yr. For the model plant burning of the VOC in the plant emergency flare system would release about 0.02 GJ/hr as heat to the environment.

b. Catalyst Mix-Tank Scrubber Vent—The control method previously described for reduction of VOC emission from the catalyst mix-tank scrubber vent consists of installing a piping manifold to deliver this vent gas to the plant emergency flare. Use of this method would reduce VOC emissions from the model plant by about 33.3 Mg/yr. For the model plant burning of the VOC in the plant emergency flare system at 95% efficiency would release about 0.166 GJ/hr as heat to the environment.

c. Wash-Decanter System Vent—The control method previously described for reduction of VOC emission from the wash-decanter system consists of installing a piping manifold to deliver the vent gas to the plant emergency flare system. Use of this method would reduce VOC emissions from the model plant by about 2.5 Mg/yr. For the model plant burning of the VOC in the plant emergency flare system at 95% efficiency would release about 0.01 GJ/hr as heat to the environment.

d. Benzene Recovery Column Vent——The control method previously described for reduction of VOC emission from the benzene recovery column consists of installing a piping manifold to deliver the vent gas to the plant emergency flare system. Use of this method would reduce the VOC emissions from the model plant by about 3.6 Mg/yr. For the model plant, burning of the VOC in the plant emergency flare system at 95% efficiency would release about 0.019 GJ/hr as heat to the environment.

e. Cumene Distillation System Vent——Because of the small amount of VOC emitted from the cumene distillation system, no control technique for reduction of VOC emissions was evaluated for normal operation.

f. D.I.P.B. Stripping System Vent——Because of the small amount of VOC emitted from the D.I.P.B. stripping system, no control technique for reduction of VOC emissions was evaluated for normal operation.

b. Fugitive Emissions——The control methods previously described for these emissions are major leak detection and correction as described in Appendix C. Application of these methods would result in a VOC emission reduction of 83.2 Mg/yr for the model plant.

h. Storage and Handling[7]——The control method previously described for reduction of VOC emissions from storage tanks consists of installing floating roofs on tanks handling benzene or organic mixtures containing benzene. Application of this method to the model plant would reduce emissions by about 177 Mg/yr.

i. 1978 Industrial Emissions——It has been estimated that the current industrial capacity for manufacture of cumene by the aluminum chloride catalyst process is 400 Gg/yr. Using the figure of 57% for capacity utilization, this amounts to a production level of 230 Gg in 1978. For the uncontrolled model plant at 227 Gg/yr the emission level is 440 Mg/yr. For the controlled model plant at 227 Gg/yr the emission level is 130 Mg/yr. It has been estimated that the actual emissions from cumene manufacture by the aluminum chloride catalyst process were 180 Mg in 1978 (assuming current control at 85% of the level specified for control of the model plant).

B. CONTROL COST IMPACT

Details of the model plants (Figs. III-1 and III-2) are given in Sect. III and control techniques are discussed in Sect. IV.

1. Solid Phosphoric Acid Catalyst Process

a. Cumene Distillation System Vent—The VOC emissions from this vent are relatively small. The only technique that seemed reasonable was to inject this vent gas into the manifold leading to the plant emergency flare system. The cost impact of connecting the cumene distillation system vent to the flare manifold is negligible when a new plant is being designed. The cost of retrofitting this control to an existing plant may be appreciably greater than the cost for a new installation if there is some distance between the source and the existing flare manifold.

b. Fugitive Emission Sources—A control system for fugitive sources is defined in Appendix C. A separate EPA report covers fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[9]

c. Storage and Handling Sources—The use of floating roofs on tanks handling benzene or mixtures containing benzene has been selected as the technique for reduction of VOC emissions from the model plant. No economic evaluation or cost-benefit analysis for floating-roof versus fixed-roof tanks has been prepared for this report. The economics for floating-roof versus fixed- roof storage tanks is covered in a separate EPA report.[10]

2. Aluminum Chloride Catalyst Process[8]

a. Process Vents—The control technique that was selected for all the process vents was to inject the vent gas into the manifold leading to the plant emergency flare system. The cost impact of connecting these vents to the flare manifold is negligible when a new plant is being designed. The cost of retrofitting this control to an existing plant may be appreciably greater than the cost for a new installation if there is some distance between the sources and the existing flare manifold.

b. Cumene Distillation System Vent—The VOC emissions from this vent during normal operation are very small, and no control system was evaluated.

c. D.I.P.B. Stripping System Vent—The VOC emissions from this vent during normal operation are very small, and no control system was evaluated.

d. Fugitive Emission Sources—A control system for fugitive emission sources is defined in Appendix C. A separate EPA report covers fugitive emissions and their applicable controls for the synthetic organic chemical manufacturing industry.[9]

e. Storage and Handling Sources[7,9]—The use of floating roofs on tanks handling benzene or mixtures containing benzene has been recommended as the technique for reduction of VOC remissions from this model plant. No economic evaluation or cost-benefit analysis for floating-roof versus fixed-roof tanks has been prepared for this report. The economics for fixed-roof versus floating-roof storage tanks are covered in a separate EPA report.[10]

C. REFERENCES*

1. Y. C. Yen, Phenol, Supplement A, pp. 19—41, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (September 1972).

2. J. R. Kampfhenkel, letter dated Sept. 12, 1978, to EPA from Sun Petroleum Products Co., Corpus Christi, TX, in response to EPA's request for information on the cumene process.

3. M. P. Zanotti, letter dated Sept. 19, 1978, to EPA from Gulf Oil Co., Port Arthur, TX, in response to EPA's request for information the cumene process.

4. Oliver J. Zandona, letter dated Sept. 25, 1978, to EPA from Ashland Petroleum Co., Ashland, KY, in response to EPA's reuqest for information on the cumene process.

5. Michael A. Pierle, letter dated Oct. 23, 1978, to EPA from Monsanto Chemical Co., St. Louis, MO, in response to EPA's request for information on the cumene process.

6. Attachment II, Information on the Cumene Process, from Shell Oil Co., Deer Park, TX, in response to EPA's request for information on the cumene process.

7. C. C. Masser, "Storage of Petroleum Liquids," Sect. 4.3 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

8. F. D. Bess, letter dated Sept. 21, 1978, to EPA from Union Carbide Corp., South Charleston, WV, in response to EPA's request for information on the cumene process.

9. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

10. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Cumene is manufactured domestically by the alkylation of benzene with propylene. The two processes of commercial significance use different catalysts and operating conditions to promote the alkylation reaction. Domestic production of cumene (including Puerto Rico) was estimated to be 1257 Gg in 1978, with an estimated total plant capacity of 2194 Gg/yr, giving an industrial capacity utilization rate of 57%. The principal domestic use of cumene is in the manufacture of phenol, along with co-product acetone, by the cumene hydroperoxide process. The estimated annual growth rate for cumene manufacture is 4.4%/yr.

Emission sources along with uncontrolled and controlled air emission rates for the solid phosphoric acid catalyst model-plant process for cumene manufacture are given in Table VII-1. The comparable sources and values for the aluminum chloride catalyst model-plant process for cumene manufacture are given in Table VII-2.

None of the process-generated VOC emissions from the solid phosphoric acid catalyst process or from the aluminum chloride catalyst process are very large. The technique that was evaluated for controlling these emissions would be to collect them in a piping system and to inject the collected vent gases into the manifold header leading to the plant emergency flare for thermal destruction. The largest and most significant VOC emissions are released by storage tanks handling benzene. The use of floating roofs on storage tanks handling benzene is the preferred way to control these sources of VOC emissions.

The average level of control for VOC emissions from existing cumene manufacturing plants is estimated to be at least 85% of the control level for the controlled emission model plants. At this estimated level of control the 1978 total level of VOC emissions is estimated to be about 380 Mg/yr.

The solid phosphoric acid process is preferred by most of the manufacturers of cumene, since it can use a crude propylene stream from an adjacent refinery cracker, as well as refined benzene from the same adjacent refinery. The solid phosphoric acid catalyst is selective for alkylation of benzene with propylene, with a minimum of other alkylbenzenes being generated. A fairly large purge

Table VII-1. Emission Summary for Model Plant Producing Cumene by Process Using Solid Phosphoric Acid Catalyst (227 Gg/yr)

Emission Source	Stream Designation (Fig. III-1)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
Cumene distillation system	A_3	0.9	0.05
Fugitive		6.3	1.8
Storage and handling		7.1	1.94
Secondary		0.2	0.2
Total		14.5	3.99

Table VII-2. Emission Summary for Model Plant Producing Cumene by Process Using Aluminum Chloride Catalyst (227 Gg/yr)

Emission Source	Stream Designation (Fig. III-2)	VOC Emission Rate (kg/hr)	
		Uncontrolled	Controlled
Benzene azeotrope drying column	A_1	0.54	0.027
Catalyst mix tank scrubber vent	A_2	4.0	0.20
Wash-decanter system	A_3	0.3	0.015
Benzene recovery column	A_4	0.43	0.022
Cumene distillation system	A_5	0.07	0.07
D.I.P.B. stripping column	A_6	0.02	0.02
Fugitive		13.3	3.79
Storage and handling		25.1	4.83
Secondary		6.0	6.0
Total		49.8	15.0

stream of recovered benzene is returned to the refinery to remove impurities from the cumene plant recycle stream. The crude propane left over after the propylene is extracted is also returned to the refinery. Because of the close links to refinery operation, this solid phosphoric acid catalyst process is economically attractive only when closely associated with an adjacent refinery. It is estimated that the total cumene capacity by this route is about 1750 Gg/yr, or about 80% of the total domestic cumene capacity.

The aluminum chloride catalyst process is preferred by a few manufacturers of cumene, since it uses chemical-grade propylene (about 95% purity) and refined benzene. Feedstock costs are higher for chemical-grade propylene than for a crude refinery stream, but the amount of propane and other contaminants that must be handled and rejected by this process is much lower than the amount of those in the gas stream rejected by the solid phosphoric acid process. This aluminum chloride process does not require close linkage to a refinery operation, but can function as an independent plant. The by-product diisopropylbenzene formed in this process can be recycled back to the reaction section for transalkylation with excess benzene to form additional cumene, thereby increasing yields. It is estimated that the total cumene capacity by this route is about 400 Gg/yr, or about 20% of the total domestic cumene capacity.

APPENDIX A

Table A-1. Physical Properties*

Material	Formula	Molecular Weight	Boiling Point (°C)	Freezing Point (°C)	Specific Gravity, 20/4°C of Liquid	Gross Heat of Combustion (MJ/kg)
Propane	C_3H_8	44.1	-44.5	-189.9	0.508	50.4
Propylene	C_3H_6	42.1	-47.8	-185.2	0.522	48.9
Benzene	C_6H_6	78.1	80.1	5.5	0.878	41.8
Ethylbenzene	C_8H_{10}	106.2	136.2	-94.9	0.867	43.0
Cumene	C_9H_{12}	120.2	152.4	-96.0	0.866	43.4
_m_-Diisopropylbenzene	$C_{12}H_{18}$	162.3	203	-63.0	0.856	45.5
_p_-Diisopropylbenzene	$C_{12}H_{18}$	162.3	210	-17	0.857	45.5

*Values abstracted from J. B. Maxwell, _Data Book on Hydrocarbons_, Van Nostrand, New York City, 1955, and from R. C. Weast _et al_., _Handbook of Chemistry and Physics_, The Chemical Rubber Co., Cleveland, 1964.

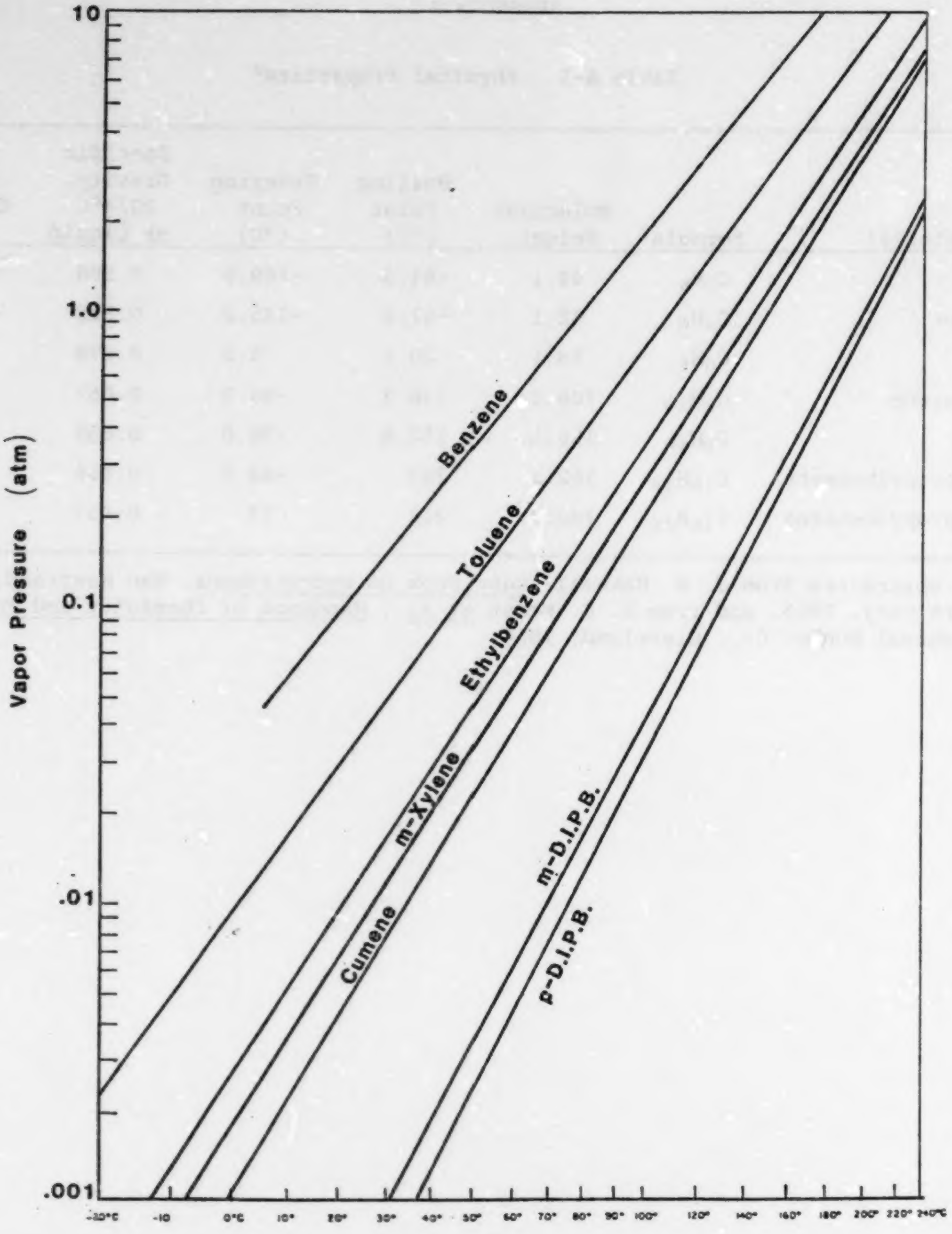

Fig. A-1. Vapor Pressure vs Temperature

APPENDIX B

Table B-1. Air-Dispersion Parameters for Model Plant Producing Cumene by Process Using Solid Phosphoric Acid Catalyst and with a Capacity of 227 Gg/yr

Emission Source	Stream Designation (Fig. III-1)	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Total Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled				
Cumene distillation system vent	A_3	0.25	27	0.025	322	0.0008	1.6
Fugitive[a]		1.76			322		
Storage and handling		1.98			293		
Secondary		0.056			298		
			Controlled				
Cumene distillation system vent	A_3	0.013	73	Unknown	1250[b]	Variable	Variable[c]
Fugitive[a]		0.50			322		
Storage and handling		0.25			293		
Secondary		0.056			298		

[a] Fugitive emissions are distributed over an area of about 200 m by 300 m.

[b] Minimum.

[c] 1.2 minimum.

Table B-2. Air-Dispersion Parameters for Model Plant Producing Cumene by Process Using Aluminum Chloride Catalyst (Capacity, 227 Gg/yr)

Source	Stream Designation (Fig. III-2)	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Total Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled				
Benzene azeotrope drying column	A_1	0.15	36	0.025	322	0.00060	1.2
Catalyst mix tank scrubber	A_2	1.11	36	0.076	293	0.00449	1.0
Wash-decanter system	A_3	0.083	36	0.038	293	0.00118	1.0
Benzene recovery column	A_4	0.119	36	0.025	322	0.00053	1.0
Cumene distillation system	A_5	0.0194	36	0.064	322	0.0206	6.5
D.I.P.B. stripping system	A_6	0.006	36	0.025	322	0.00030	0.6
Fugitive*		3.69					
Storage and handling		6.97					
Secondary		1.667					
			Controlled				
Benzene azeotrope drying column	A_1	0.0075	73	Unknown	1250 min	Variable	Variable (1.2 min)
Catalyst mix tank scrubber	A_2	0.0556	73	Unknown	1250 min	Variable	Variable (1.2 min)
Wash-decanter system	A_3	0.0042	73	Unknown	1250 min	Variable	Variable (1.2 min)
Benzene recovery column	A_4	0.0061	73	Unknown	1250 min	Variable	Variable (1.2 min)
Cumene distillation system	A_5	0.0194	36	0.064	322	0.0206	6.5
D.I.P.B. stripping system	A_6	0.0056	36	0.025	322	0.00030	0.6
Fugitive*		1.053					
Storage and handling		1.34					
Secondary		1.667					

*Fugitive emissions are distributed over an area of about 200 m by 300 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr-source)	Controlled Emission Factor[a] (kg/hr-source)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed to correct leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, Radian Corporation, EPA 600/2-79-044 (February 1979).

APPENDIX D

EXISTING PLANT CONSIDERATIONS

A. CHARACTERIZATION

Table D-1 lists the emission control techniques reported in use by industry. Sources of information in this appendix are letters in response to requests by EPA for information on emissions from cumene plants.[1—6]

B. RETROFITTING CONTROLS

The primary difficulty with retrofitting the controls described in this report is that the distances between the vents and the manifold to the emergency flare may be so great that the cost of connecting the vents to the existing manifold may be appreciably more than the cost of connecting the vents to the flare manifold during construction of a new plant.

Table D-1. Emission Control Devices or Techniques Currently Used by Some Cumene Producers[a]

Emission Source	Stream Designation	Control Devices or Techniques Used					
		By Ashland Oil Company	By Gulf Oil Company	By Monsanto Chemical Company	By Shell Oil Company	By Sun Petroleum Products Company	By Union Carbide Corporation
				Solid Phosphoric Acid Catalyst Process (Fig. III-1)			
Propane recovery system vent	A_1	Vent to propane gas manifold	Vent to propane gas manifold	Vent to propane gas manifold	Vent to fuel gas manifold[b]	Vent to propane gas manifold	
Benzene recovery system vent	A_2	Vent to plant flare	Vent to plant flare	Vent to atmosphere through vent condenser	Vent to fuel gas manifold[b]	Vent to plant flare	
Cumene distillation system vent	A_3	Vent to plant flare	Vent to atmosphere	Vent to atmosphere	Vent to fuel gas manifold[b]	Vent to atmosphere	
				Aluminum Chloride Catalyst Process (Fig. III-2)			
Benzene azeotrope drying column	A_1						Through vent header and collection pot to atmosphere[c]
Catalyst mix tank scrubber	A_2						Vent to atmosphere
Wash-decanter system	A_3						Vent through degasser and gas wash system to propane gas manifold
Benzene recovery column	A_4						Through vent header and collection pot to atmosphere[c]
Cumene distillation system	A_5						Through vent header and collection pot to atmosphere[c]
D.I.P.B. stripping system	A_6						Through vent header and collection pot to atmosphere[c]
				Auxiliary Sources			
Fugitive		Unknown	Unknown	Unknown	Unknown	Unknown	Unknown
Storage and handling		Unknown	Unknown	Floating roof on benzene storage tank	Unknown	Unknown	Unknown
Secondary		Small wastewater (syrup) stream with no oil layer; sent to plant sewer	Waste water decanted to remove oil layer; then sent to plant biooxidation system	Wastewater sent to general plant chemical sewer line for deep-well injection	Wastewater decanted to remove oil layer; then sent to plant biooxidation system	Tars steam-stripped and volatiles sent to flare; wastewater decanted to remove oil layer and then sent to plant biooxidation system	Wastewater decanted to remove oil layer; then sent to plant wastewater treatment system

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[a] From refs 1—6.

[b] Excess fuel gas over manifold capacity diverted to plant flare.

stillation columns operated under pressure with high-pressure shutdown controls; manufacturer claims no venting of organics to vent header and collection pot under normal operating
tions.

C. REFERENCES*

1. J. R. Kampfhenkel, letter dated Sept. 12, 1978, to EPA from Sun Petroleum Products Co., Corpus Christi, TX, in response to EPA's request for information on the cumene process.

2. M. P. Zanotti, letter dated Sept. 19, 1978, to EPA from Gulf Oil Co., Port Arthur, TX, in response to EPA's request for information on the cumene process.

3. Oliver J. Zandona, letter dated Sept. 25, 1978, to EPA from Ashland Petroleum Co., Ashland, KY, in response to EPA's request for information on the cumene process.

4. Michael A. Pierle, letter dated Oct. 23, 1978, to EPA from Monsanto Chemical Co., St. Louis, MO, in response to EPA's request for information on the cumene process.

5. Attachment II, Information on the Cumene Process, from Shell Oil Co., Deer Park, TX, in response to EPA's request for information on the cumene process.

6. F. D. Bess, letter dated Sept. 21, 1978, to EPA from Union Carbide Corp., South Charleston, WV, in response to EPA's request for information on the cumene process.

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REPORT 4

TOLUENE DIISOCYANATE

David M. Pitts

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. TOLUENE DIISOCYANATE

Toluene diisocyanate (TDI) production was selected for study because preliminary estimates indicated that emissions of volatile organic compounds (VOC) and the potential toxicity of the chlorinated hydrocarbon raw materials were relatively high.

TDI is the most important diisocyanate for the production of polyurethane materials. The bulk of commercially used TDI is a mixture of 80 parts of the 2,4-isomer and 20 parts of the 2,6-isomer. Pertinent physical properties of TDI are given in Appendix A. A 65:35 mixture of the 2,4- and 2,6-TDI isomers is also available commerically, as is the pure 2,4-isomer. They are not, however, widely used. TDI is produced by the phosgenation of toluene diamine, which is manufactured by the reduction of dinitrotoluene, which in turn is produced by the nitration of toluene. Either nitration-grade toluene or highly refined toluene (99.95+%) is used as the basic feed stock by most TDI manufacturers.[1]

B. TDI USAGE AND GROWTH

The total domestic consumption of TDI in 1977 was 265 Gg, with the following breakdown in usage: foams, 185 Gg; coatings, 12.7 Gg; elastomers 5.9 Gg; other uses, 3.2 Gg; exports, 58.2 Gg. The total consumption of TDI in 1982 is estimated to be 300 to 322 Gg, which represents an estimated annual growth rate of 2.6 to 4.3%.[1]

Overall demand for flexible foams is expected to increase only modestly, with the major growth in uses for bedding and underpadding. The demand for TDI for uses in rigid foams for insulation in refrigerators and freezers is not expected to grow because of the increasing use of polymeric isocyanates in this application.[1]

It is a matter of speculation as to whether the use of fluorocarbons in flexible foam production will be banned and what the effects of such a ban would be on the flexible foam industry and therefore on the demand for TDI. More TDI might be required if fluorocarbons are not used in the foam manufacture, but this more expensive foam may have a decreased market demand.[1]

The consumption of TDI for use in commercial and industrial coating systems is projected to grow at a rate of 5—7% per year.

The use of TDI for elastomers and similar products is projected to grow at an annual rate of 3 to 5%. Other uses include foundry core binders, fabric coatings, adhesives and sealants, injection-molding resins, millable gums, and fibers.[1]

Exports of TDI are not expected to increase above 1977 levels and may even decline slightly as output of the large new Bayer plant at Brunebuettel, Federal Republic of Germany, continues to be used in export markets.[1]

C. DOMESTIC PRODUCERS

There are eight major producers of TDI in the United States at ten plants. Table II-1 lists the producers, plant locations, and overall annual capacities as of January 1978 for each company.[1] In the latter part of 1978 the 25-Gg/yr Union Carbide facility at Institute, West Virginia, was shut down,[2] making the total TDI annual production capacity at 340.5 Gg at the end of 1978. Normally plants operate at 80 to 85% of nameplate capacity[3] and additional capacity may be required before 1982.

Table II-1. TDI Producers, Locations, and Capacities[a]

Company	Plant Location	Annual Capacity (Gg/yr)
Mobay Chemical Corp.	Cedar Bayou, TX	59.0
	New Martinsville, WV	45.4
Olin Corp.	Ashtabula, OH	13.6
	Lake Charles, LA	45.4
BASF Wyandotte	Giesmar, LA	45.4
Dow Chemical USA	Freeport, TX	45.4
Allied Chemical Corp.	Moundsville, WV	36.3
Du Pont	Deepwater Point, NJ	31.8
Union Carbide [b]	Institute	25.0
Rubicon Chemicals	Geismar, LA	18.2
Total		365.5

[a] See ref 1.

[b] This plant was closed in the latter part of 1978.

D. REFERENCES*

1. H. E. Frey and Andrew J. Wolfe, "Diisocyanates and Polyisocyanates," pp. 666.5021A—666.5023B in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (September 1978).

2. Telephone conversation, March 1979, between John Bresland, Allied Chemical, and David M. Pitts, IT Enviroscience, Inc.

3. "Chemical Profile on TDI," in Chemical Marketing Reporter, Feb. 14, 1977.

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. PROCESS DESCRIPTION

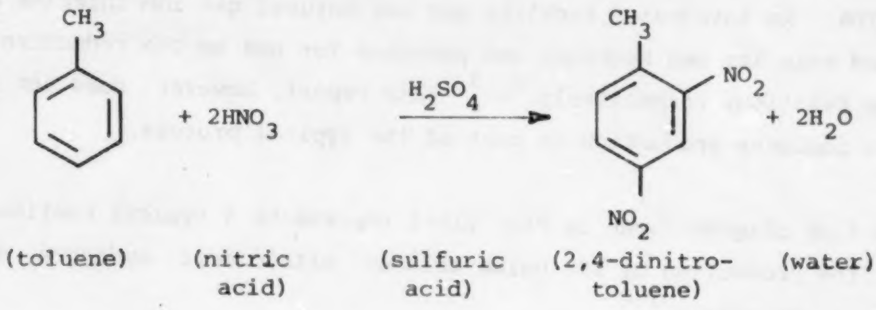
A. INTRODUCTION

The manufacture of commercial toluene disocyanate is based on the phosgenation of primary amines. As stated previously most commercial TDI plants are integrated with the production of the intermediates dinitrotoluene (DNT), toluene diamine (TDA) and phosgene.[1—3]

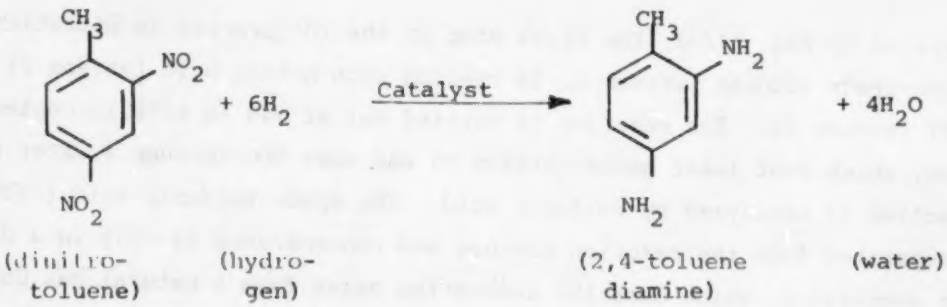
B. TYPICAL PROCESS FOR THE PRODUCTION OF TDI

TDI is produced by the following chemical reactions:

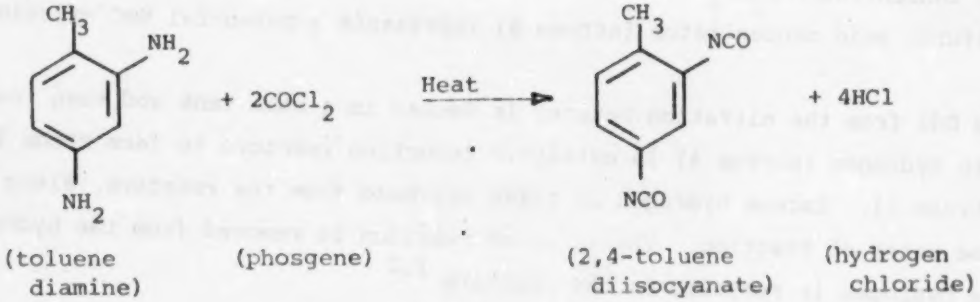
Reaction 1:


CH3
+ 2HNO3
H2SO4
CH3
NO2
+ 2H2O
NO2
(toluene)
(nitric acid)
(sulfuric acid)
(2,4-dinitro-toluene)
(water)

Reaction 2:


CH3
NO2
NO2
+ 6H2
Catalyst
CH3
NH2
NH2
+ 4H2O
(dinitro-toluene)
(hydro-gen)
(2,4-toluene diamine)
(water)

Reaction 3:


CH3
NH2
NH2
+ 2COCl2
Heat
CH3
NCO
NCO
+ 4HCl
(toluene diamine)
(phosgene)
(2,4-toluene diisocyanate)
(hydrogen chloride)

The nitration product (Reaction 1) typically contains 80% 2,4-dinitrotoluene isomers and 20% 2,6-dinitrotoluene isomer. Other isomers (2,3- and 3,4-dinitrotoluene) and some unreacted toluene and nitrotoluene may be present in small amounts. To simplify presentation the formula is shown as the 2,4-isomer only.[3]

The phosgenation reaction (Reaction 3) is carried out using either monochloro- or *o*-dichlorobenzene as a solvent. Approximately 0.7 lb of toluene and 1.3 lb of phosgene are consumed for each pound of distilled 80:20 TDI produced. Hydrochloric acid is the only useful by-product produced, about 0.8 lb per pound of TDI.[3]

The typical TDI plant operates continuously and is integrated with the production of DNT and TDA. An integrated facility may use natural gas and chlorine as raw materials and make its own hydrogen and phosgene for use in the reduction and phosgenation reactions respectively.[1—3] This report, however, does not include hydrogen and phosgene production as part of the typical process.

The process flow diagram shown in Fig. III-1 represents a typical continuous process for the production of TDI using toluene, nitric acid, hydrogen, and phosgene as raw materials.[1,2]

As indicated by Fig. III-1, the first step of the TDI process is nitration. Nitration-grade toluene (stream 1) is reacted with nitric acid (stream 2) to form DNT (stream 3). The reaction is carried out at ~49 to 66°C in cooled reactors, which vent inert gases (stream C) and some VOC through a water scrubber. The reaction is catalyzed by sulfuric acid. The spent sulfuric acid (~70%) is phase separated from the reaction mixture and concentrated to ~93% in a direct-contact evaporator, which uses the combustion gases from a natural gas burner. The concentrated H_2SO_4 solution is recycled to the reactor. The vent from the sulfuric acid concentrator (stream B) represents a potential VOC emission.

The DNT from the nitration reactor is washed in a wash tank and then reacted with hydrogen (stream 4) in catalytic reduction reactors to form crude TDA (stream 5). Excess hydrogen is taken overhead from the reactors, along with some water of reaction. The water of reaction is removed from the hydrogen and the hydrogen is recycled to the reactors.[1,2]

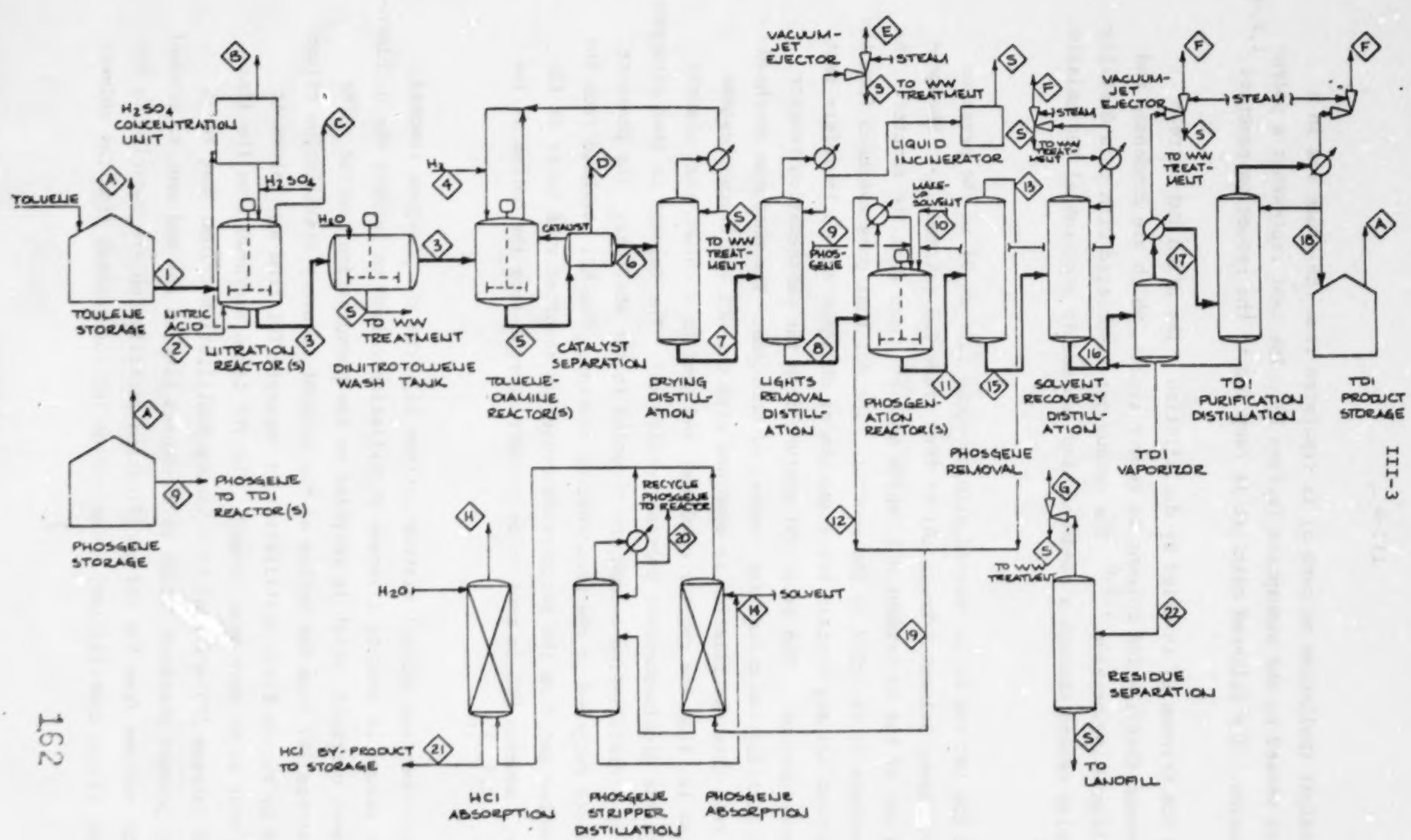

TOLUENE
A
TOULENE STORAGE
1
NITRIC ACID
2
B
H₂SO₄ CONCENTRATION UNIT
C
H₂SO₄
NITRATION REACTOR(S)
3
H₂O
DINITROTOLUENE WASH TANK
S
TO WW TREATMENT
3
H₂
4
TOLUENE-DIAMINE REACTOR(S)
5
CATALYST
D
CATALYST SEPARATION
6
DRYING DISTILLATION
7
S
TO WW TREATMENT
LIGHTS REMOVAL DISTILLATION
8
9
PHOSGENE
VACUUM-JET EJECTOR
E
STEAM
S
TO WW TREATMENT
LIQUID INCINERATOR
S
MAKE-UP SOLVENT
10
PHOSGENATION REACTOR(S)
11
12
13
15
PHOSGENE REMOVAL
F
STEAM
S
TO WW TREATMENT
SOLVENT RECOVERY DISTILLATION
16
TDI VAPORIZOR
17
VACUUM-JET EJECTOR
F
STEAM
S
TO WW TREATMENT
TDI PURIFICATION DISTILLATION
18
F
A
TDI PRODUCT STORAGE
A
PHOSGENE STORAGE
9
PHOSGENE TO TDI REACTOR(S)
H
H₂O
HCl ABSORPTION
21
HCl BY-PRODUCT TO STORAGE
RECYCLE PHOSGENE TO REACTOR
20
PHOSGENE STRIPPER DISTILLATION
SOLVENT
14
PHOSGENE ABSORPTION
19
G
S
TO WW TREATMENT
22
RESIDUE SEPARATION
S
TO LANDFILL

Fig. III-1. Process Flow Diagram for Uncontrolled Integrated TDI Plant

The solid catalyst (palladium on carbon) is separated from the crude TDA in a filter that is vented to the atmosphere (stream D). The vent represents a potential VOC emission. The filtered catalyst is recycled to the reduction reactors.[1,2,4]

The filtered TDA (stream 6) is dried by distillation. The dried TDA (stream 7) is sent to vacuum distillation columns to remove lights, which are condensed and burned in a liquid incinerator.[1,2,4] The vacuum jet associated with this distillation is normally vented through a condenser and represents a potential VOC emission (stream E).[2]

The purified TDA (stream 8) is reacted with phosgene (stream 9) in the presence of *o*-dichlorobenzene solvent (stream 10) to form crude TDI (stream 11). Phosgene is condensed out of the by-product HCl, which goes overhead from the reactor. The condensed phosgene is recycled to the reactor. The HCl that goes overhead from the condenser (stream 12) may contain trace amounts of phosgene and is therefore sent to the phosgene absorber. The crude TDI mixture from the phosgenation reactor is sent to a distillation column for removal of phosgene. The phosgene overhead (stream 13) from this distillation is combined with the HCl and trace-phosgene stream (stream 12) from the reactor condenser and sent to a column that absorbs phosgene with the dichlorobenzene solvent (stream 14). The solvent is then stripped of phosgene in a distillation column and recycled to the absorber. The phosgene is condensed and recycled to the phosgenation reactor. The HCl overhead from the phosgene absorber and from the stripper condenser is absorbed with water in the HCl absorber. Aqueous HCl is sent to by-product storage from the bottom of the HCl absorber.[1,2,4–7]

The TDI-dichlorobenzene solvent mixture (stream 15) from the phosgene removal distillation column is sent to a vacuum distillation column to recover the dichlorobenzene solvent overhead, which is recycled to the phosgenation reactor. The crude TDI (stream 16) from the bottom of the solvent recovery distillation column is vaporized by vacuum flash distillation to separate TDI from any polymeric isocyanates that might have been formed. The TDI taken overhead from the flash is condensed (stream 17) and sent to a vacuum distillation column that takes purified TDI product overhead, which is condensed (stream 18) and sent to product storage. The bottoms from the TDI purification distillation are recycled to the TDI vaporizer (flash distillation). The vacuum jet condensates from the solvent recovery distillation, from the flash distillation, and from the TDI purification distillation are sent to wastewater treatment. The bottoms from the TDI vaporizer (stream 22) are sent to a vacuum distillation column, which separates the polymeric isocyanate residue from any comparatively low boiling compounds that might be contained in the residue. The residue from the bottom of this separation column is sent to landfill. The vacuum jet condensate from this distillation is also sent to wastewater treatment.[1,2,4_7]

The residue separation vacuum jet vent (G) and the vacuum jet vents (F) associated with the solvent recovery distillation, the TDI flash distillation, and the TDI purification distillation and the HCl absorber vent (H) represent potential sources of VOC emissions.[2,4_7]

C. PROCESS VARIATIONS

The available data indicate the potential for significant process variations to exist among the different manufacturers with respect to the type of equipment used and the sequence of operations for a given process step. Major process differences reflect differences in raw materials. In some cases dinitrotoluene is purchased, obviating the requirement for toluene nitration and thus eliminating the H_2SO_4 concentration unit. At least one manufacturer (Olin) purchases toluene diamine, thus eliminating the TDA reaction step. It is known that at least one manufacturer (Allied) makes phosgene as part of the integrated TDI facility.

Very limited data indicate differences in the TDI recovery, purification, and residue recovery steps although no significant details are available. All TDI recovery and purification steps, however, should require vacuum distillation and/or evaporation steps, which would give rise to similar types of VOC emissions.[1,2,4_7]

D. OTHER PROCESSES

Mitsui Toatsu Chemicals, Inc., in Japan has developed a TDI process based on dinitrotoluene carbonylation. In this process, dinitrotoluene is catalytically carbonylated in the presence of an alcohol to give diurethane intermediate, which is then thermally decomposed to TDI. The absence of a phosgenation step is the principal difference between the Japanese process and the current commercial process. Mitsui has announced plans to build a 50-Gg/yr TDI plant in Japan using this process, to be completed in 1980.[3] This report, however, covers only the present commerical process.

E. REFERENCES*

1. Yen-Chen Yen, Isocyanates Supplement B, Report No. 1B, Process Economics Program, Stanford Research Institute, Menlo Park, CA (November 1973).

2. David M. Pitts, IT Enviroscience, Inc., Trip Report on Site Visit to Allied Chemical Corp., Morristown, NJ, Mar. 15, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. H. E. Frey and Andrew J. Wolfe, "Diisocyanates and Polyisocyanates," pp. 666-5021A—666-5023B in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (September 1978).

4. T. R. Kovacevich, BASF Wyandotte Corp., letter dated May 31, 1978, regarding toluene diisocyanate process at the Geismar plant, in response to EPA's request for information on emissions data from TDO production facilities.

5. Donald W. Smith, E. I. du Pont de Nemours & Co., letter dated May 17, 1978, regarding toluene diisocyanate process at Chambers Works, in response to EPA's request for information on emissions data from TDO production facilities.

6. Lee P. Hughes, Mobay Chemical Corp., letter dated May 3, 1978, regarding the toluene diisocynate process at Cedar Bayou plant, in response to EPA's request for information on emissions data from TDO production facilities.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. TYPICAL PLANT

The capacity of the typical integrated plant for the production of TDI developed for this study is 45 Gg/yr, based on 8760* hr of production annually. Although not an actual operating facility, the size of the plant is typical of most present industrial operating units using the typical process described in Sect. III.

B. PROCESS SOURCES AND EMISSIONS

As indicated in Section III, there are nine potential sources of process emissions (labeled B-H in Fig. III-1) in the manufacture of TDI by the typical process considered in this report. Uncontrolled process emissions have been calculated for the most part from estimated and measured data on controlled emissions and estimated control efficiencies provided by the Allied Chemical Corporation[1] and from process and emission data from other sources.[2—6] These estimated uncontrolled process emissions are summarized in Table IV-1.

Storage and handling, fugitive, and secondary emissions are not considered in the abbreviated report but they are covered for the entire synthetic organic manufacturing industry by separate EPA documents. For convenience, sources of storage emissions are labeled A and potential sources of secondary emissions are labeled S in Fig. III-1.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

As indicated by Table IV-1, the most significant uncontrolled VOC emission from TDI manufacturing (vent B in Table III-1) results from the H_2SO_4 concentration unit. This unit uses hot combustion gases to evaporate water from the spent H_2SO_4 solution coming from the nitration reactors. The estimated uncontrolled composition given in Table IV-2 for this vent stream was calculated from data on controlled emissions and estimated control efficiencies provided by the Allied Chemical Corporation.[1]

Vent C represents the emissions from the nitration reactors and contains inert gases (mostly air), SO_2, NO_x, and small amounts of nitroaromatic compounds.[1]

Vent D represents the emissions from the TDA reactors via the catalyst separation unit and contains air and small amounts of organic amines.[1,3]

Vent E represents the emissions from the vacuum jet associated with the distillation to remove low-boiling organic amines from the TDA. The air that is discharged through the vacuum-jet hot well carries some of these light organic amines with it.[1,3]

Vents F represent the emissions from the vacuum-jet hot wells associated with the dichlorobenzene solvent recovery distillation, the TDI flash distillation, and the TDI purification distillation. These vents taken together represent the second most significant uncontrolled VOC emission from the typical TDI plant according to estimated data from Allied.[1] No detailed composition data on these streams are available although it has been estimated, based on other industry data,[3—6] that the major VOC component of the combined uncontrolled emission is phosgene (~99%) and that the remainder of the VOC is dichlorobenzene.

Vent G represents the emissions from the vacuum-jet hot well associated with the residue separation distillation. This emission contains mostly air and trace amounts of chlorinated hydrocarbons, which can be formed from the phosgenation reaction.[1,3—6]

Table IV-1. Summary of Uncontrolled Process Emissions from Typical TDI Process Plant

Source	Stream Designation (Fig.III-1)	VOC Emissions Ratio (g/kg)*	VOC Emissions Rate (kg/hr)
H_2SO_4 concentrator	B	5.0	25.90
Nitration reactor(s)	C	0.025	0.13
TDA reaction via catalyst filtration	D	0.0005	0.0026
TDA lights removal distillation	E	0.0033	0.017
Solvent recovery, flash, and product purification distillations	F	4.6	23.8
Residue separation	G	1.1×10^{-5}	5.7×10^{-5}
HCl absorber	H	4.6×10^{-7}	2.4×10^{-6}
Total process emissions		9.63	49.8

*g of VOC per kg of TDI produced.

Table IV-2. Estimated Typical Composition of Gas from the H_2SO_4 Concentration Unit (Vent B)

Component	Composition (wt %)
Combustion products and H_2O vapor	99.68
SO_2	0.005
NO_x	0.06
H_2SO_4	0.18
Nitroaromatics	0.075
Total	100

Vent H represents the emissions from the HCl absorber and contains small amounts of phosgene in the CO_2 and water vapor discharged from the acid recovery system.[1,3–6]

It should be noted that phosgene represents a large percentage (~99%) of the estimated uncontrolled VOC emissions associated with the solvent recovery and TDI product distillations. Because of its toxicity, emissions of phosgene must be controlled to extremely low levels.

C. REFERENCES*

1. David M. Pitts, IT Enviroscience, Inc., Trip Report on Site Visit to Allied Chemical Corp., Morristown, NJ, Mar. 15, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. H. E. Frey and Andrew J. Wolfe, "Diisocyanates and Polyisocyanates," pp. 666-5021A—666-5023B in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (September 1978).

3. T. R. Kovacevich, BASF Wyandotte Corp., letter dated May 31, 1978, regarding toluene diisocyanate process at the Geismar plant, in response to EPA's request for information on emissions data from TDI production facilities.

4. Donald W. Smith, E. I. du Pont de Nemours & Co., letter dated May 17, 1978, regarding toluene diisocyanate process at Chembers Works, in response to EPA's request for information of emissions data from TDI production facilities.

5. Lee P. Hughes, Mobay Chemical Corp., letter dated May 3, 1978, regarding toluene diisocyanate process at Cedar Bayou plant, in response to EPA's request for information on emissions data from TDI production facilities.

6. J. C. Ketchum, Union Carbide Corp., letter dated May 16, 1978, regarding toluene diisocyanate process at the Institute plant, in response to EPA's request for information on emissions data from TDO production facilities.

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V. APPLICABLE CONTROL SYSTEMS

A. PROCESS EMISSION CONTROLS FOR TYPICAL PLANTS

Table V-1 shows the control devices, estimated VOC reduction efficiencies, and resulting emissions for each of the vent streams shown in Fig. III-1 and discussed in Sect. IV. The control devices used and the estimated reduction efficiencies represent nonconfidential data obtained from one company.[1] Based on limited information from other sources,[2—6] the data given in Table V-1 are felt to be representative of the TDI industry in general. The cost and cost effectiveness for these applications have not been determined.

With respect to the sulfuric acid concentrator and the nitration reactor vents (B and C) the primary function of the wet scrubber control devices is to remove H_2SO_4. These devices, however, have been estimated to be ~60 to 80% efficient for removing VOC because of the nature of the nitro-organic compounds being scrubbed.[1]

With respect to the necessary control of phosgene emissions from vents F and H, all data indicate the use of dilute caustic and/or water (hydrolysis) scrubbing. The caustic scrubber or hydrolysis column is normally estimated to have >99% removal efficiency for phosgene.[1—6] In the case of TDI manufacture it is estimated that >98% of the other relatively high boiling VOC would be removed by condensation in the scrubbing device.[1] (Note: virtually 100% control of phosgene emissions may be required in order to protect workers from toxic concentrations in the vicinity of these vents.)

B. INDUSTRY EMISSIONS

From the data reported in Table V-1 the overall process emission ratio has been calculated to be 2.056 g of VOC per kg of TDI produced for the typical plant. This is believed to be typical of the TDI plants operating today. Storage and handling, secondary, and fugitive emissions are not included in the ratio. Comparison of the data in Table IV-1 with those in Table V-1 indicates that the TDI industry is ~78.6% controlled overall with respect to process emissions of VOC and that the major process emission results from the H_2SO_4 concentrator. From the data in Table V-1 and the estimated 1978 total TDI production of 280 Gg, the process emissions of VOC from the TDI industry have been estimated to be 0.576 Gg,

Table V-1. VOC Emissions from Controlled Process Sources in Typical TDI Plant

Source	Stream Designation (Fig.III-1)	Control Device or Technique	Estimated VOC Emission Reduction (%)	Emissions Ratio (g/kg)*	Emissions Rate (kg/hr)
H_2SO_4 concentrator	B	Wet venturi scrubber for removal of H_2SO_4	60	2.0	10.36
Nitration reactors	C	Water scrubber (spray tower) for removal of H_2SO_4	60	0.01	0.052
TDA reaction via catalyst filtration	D	Wet venturi scrubber for particulate removal	80	1.0×10^{-4}	5.2×10^{-4}
TDA lights removal distillation	E	Water-cooled surface condensers for removal of organic amines	97	1.0×10^{-4}	5.1×10^{-4}
Solvent recovery, flash, and product purification distillations	F	Dilute caustic scrubber or hydrolysis column for phosgene removal	∿99	0.046	0.24
Residue separation	G	Water-cooled surface condensers	97	3.3×10^{-7}	1.71×10^{-6}
HCl absorber	H	Packed water scrubber (hydrolysis column for control of trace phosgene)	98	9.2×10^{-9}	4.8×10^{-8}

*g of VOC per kg of TDI produced.

not including secondary, fugitive, or storage and handling emissions. When danger exists for operator exposure to highly toxic phosgene, extra precautions are required. Therefore fugitive emissions are expected to be significantly below the normal VOC fugitive emission rate for the synthetic organic chemicals manufacturing industry.

C. ASSESSMENT

As indicated in Tables IV-1 and V-1, the major emissions from the TDI process result from the H_2SO_4 concentration step. A separate EPA report specifically covers the emissions resulting from H_2SO_4 concentration units.[7]

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an *additional* reference is required for only a certain *portion* of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

APPENDIX A

Table A-1. Physical Properties of 2,4-Toluene Diisocyanate*

Synonyms	TDI, isocyanic acid, methyl phenylene ester
Molecular formula	$C_9H_6N_2O_2$
Molecular weight	174.16
Physical state	Liquid
Specific gravity	1.22 at 20°C/4°C
Vapor pressure	<0.01 mm Hg at 20°C
Boiling point	238.3°C
Melting point	19.5 - 21.5°C
Water solubility	Reacts with H_2O to produce CO_2

*From: J. Dorigan *et al*., "Toluene Diisocyanate," p. AIV-214 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A—C)*, Rev. 1, Appendix IV, MTR-7248, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties for Phosgene*

Synonyms	Carbonoxychloride, carbonylchloride, CG
Molecular formula	CCl_2O
Molecular weight	98.92
Physical state	Gas or volatile liquid
Specific gravity	1.392 at 19°C/4°C
Vapor pressure	1428 mm Hg at 25°C
Boiling point	7.56°C =
Melting point	-118°C
Water solubility	Decomposes in H_2O
Safety hazard	Disaster hazard; highly dangerous; toxic fumes

*From: J. Dorigan et al., "Phosgene, p. AIV-42 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals O-Z, Rev. 1, Appendix IV, MTR-7248, MITRE Corp.) McLean, VA (September, 1976).

REPORT 5

CRUDE TEREPHTHALIC ACID, DIMETHYL TEREPHTHALATE, AND PURIFIED THERPHTHALIC ACID

S. W. Dylewski

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

January 1981

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Production of terephthalic acid (TPA) and dimethyl terephthalate (DMT) was selected for study because of the large amounts produced and because of the significant emissions of VOC projected from their manufacture. The DMT study has been abbreviated because industry data indicate the emissions from the DMT process to be much lower than were previously estimated. The future DMT processes are expected to be based on esterification of crude TPA, which is the process generating the lowest emissions. Appendix A lists pertinent physical properties of the chemicals of significance that are involved.

B. USAGE AND GROWTH

Dimethyl terephthalate and purified terephthalic acid (P-TPA) are alternative raw materials for the manufacture of polyester products, where 1.17 g of DMT is equivalent to 1 g of P-TPA. When DMT is used, methanol is recovered and recycled to the DMT process. Table II-1 shows the end uses of DMT and P-TPA, the percentage of consumption by each end use, and the growth rate for each use from 1976 to 1981.[1]

The predominant use is in the manufacture of polyethylene terephthalate (polyester) fibers, with small percentages going to polyester films, polybutylene terephthalate resins, exports, and other uses. Polyethylene terephthalate (PET) barrier resins for carbonated beverage bottles accounted for about 0.2% in 1976; however, it is the fastest growing end use and is projected to reach 3.5 to 4% of the total demand in 1981.[1]

The 1978 domestic annual capacity is reported to be 1997 Gg of DMT and 1314 Gg of P-TPA. Production was reported to be about 61% of capacity during 1978. Based on a projected growth rate of 6.5 to 9.0% for both products the capacity utilization will reach 78 to 86% by 1982.[1—8]

P-TPA capacity was recently expanded by 53% when Amoco Chemicals dedicated its new plant in Cooper River, SC, in late 1978.[3] However, there have been no recent increases of DMT production capacity. There actually may be some shifting in capacity from DMT to P-TPA.[1,9]

Table II-1. Dimethyl Terephthalate and Purified Terephthatic Acid Usage and Growth*

End Use	Consumption (%) for 1976		Average Growth 1976—81 (%/yr)
	DMT	P-TPA	
Polyester fibers	84.2	89.2	5.5—7.5
Polyester films	8.3	3.8	8—10
Polybutylene terephthalate resins	1.4	0	14.5—19.0
PET barier resins	0.2	0.2	84—92
Miscellaneous	0.4	1.2	4.5—8.5
Exports and Inventory Building	5.5	5.6	Not available
		Average growth rate	6.5—9.0

*See ref 1.

C. DOMESTIC PRODUCERS

As of 1978 there were three active domestic producers of DMT in five locations and one domestic producer of P-TPA in two locations. Table II-2 lists the producers, locations, and capacities. Figure II-1 shows the plant locations.[1—12] Late in the writing of this report the Chemical Marketing Reporter published an estimated capacity of domestic producers that is not significantly different from that in Table II-2.[13]

1. American Hoechst

The plant is based on the Hercules/Imhausen-Witten (Hercules) process[1,4] for DMT, which proceeds from p-xylene via a methyl p-toluate intermediate rather than through a TPA intermediate. The facility was shut down in mid-1978 and may not be reopened.[5] Through a lease arrangement Hercofina is using the plant facilities and supplying Hoechst with DMT.[2]

2. E. I. du Pont de Nemours

Both operating plants produce DMT by air oxidation of p-xylene to crude TPA (C-TPA) by the Amoco process, followed by esterification of C-TPA to DMT by the Tennessee Eastman process.[4] The DMT produced is used captively in fiber production. Following expansion by the addition of a second train at its Wilmington, NC, location, the company curtailed its formerly large purchases of DMT. A 126-Gg/yr DMT plant at Gibbstown, NJ, was shut down indefinitely in 1974; the plant has been sold and will be dismantled.[1,2]

3. Eastman Kodak (Tennessee Eastman Division and Carolina Eastman Division)

Both plants use Eastman processes to produce C-TPA and DMT and use the DMT captively in their fibers and films plants.[1,2,6]

4. Hercofina (Joint Venture of Hercules and American Petrofina)

The Hercules process is used to produce DMT for the merchant market. Some TPA is produced by hydrolysis of DMT.[1] Construction was halted in 1975 on a DMT plant in Eastover, SC, which was scheduled to have a capacity of 363 Gg/yr. This plant is being redesigned and may be converted to TPA production.[1,9] Hercules is also experimenting with a new process for production of TPA and is modifying part of its Wilmington, NC, plant to include the new technology. A 68-Gg/yr DMT plant at Burlington, NJ, was shut down indefinitely in 1974.[1] The

Table II-2. Dimethyl Terephthalate and Purified Terephthalic Acid Capacity

Plant	Capacity as of 1978 (Gg/yr) DMT	Capacity as of 1978 (Gg/yr) P-TPA
American Hoechst Corp., Spartanburg, SC	73[a,b]	
E. I. du Pont de Nemours and Co., Inc.[a]		
Cape Fear (Wilmington), NC	567[c]	
Old Hickory, TN	250[c]	
Eastman Kodak Co.		
Columbia, SC	226[c]	
Kingsport, TN	281[d]	
Hercofina,[e] Wilmington, NC	600[f]	
Standard Oil (Indiana) - Amoco Chemicals[g]		
Cooper River, SC		454[h]
Decatur, AL		860[i]
	1997	1314

[a] See refs 1,4.

[b] Shut down in mid-1978; see refs 2,5.

[c] See ref 2.

[d] See ref 6.

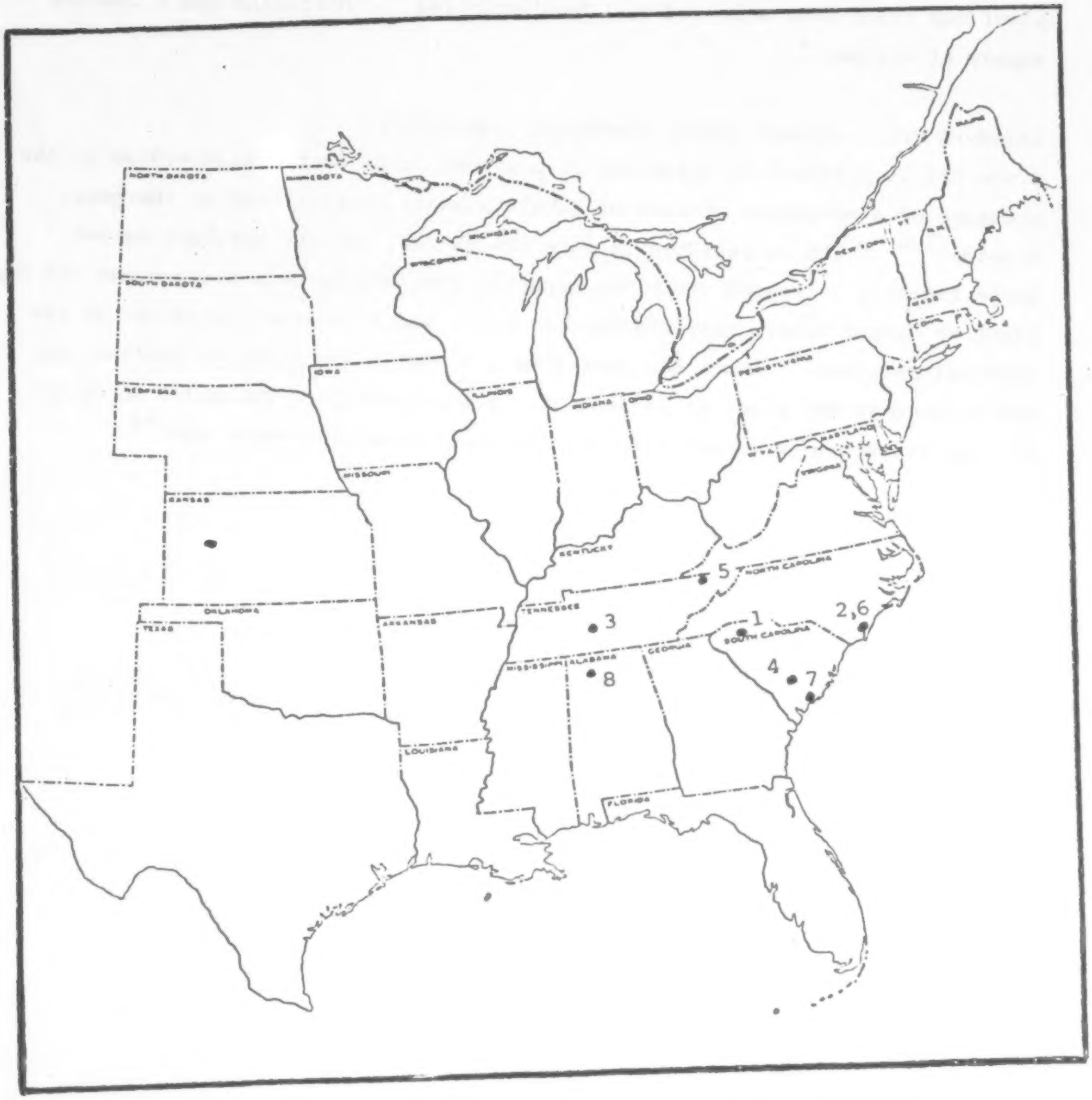
[e] See refs 1, 9, and 11.

[f] See ref 7.

[g] See ref 12.

[h] Started up late 1978; see ref 3.

[i] See ref 8.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
VT
NH
MAINE
MASS
CONN
IOWA
NEBRASKA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
MARYLAND
W VA
VIRGINIA
KANSAS
MISSOURI
KENTUCKY
NORTH CAROLINA
TENNESSEE
OKLAHOMA
TEXAS
ARKANSAS
SOUTH CAROLINA
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
5
3
1
2,6
4
7
8

1. American Hoechst, Spartanburg, SC
2. Du Pont, Cape Fear, NC
3. Du Pont, Old Hickory, TN
4. Eastman Kodak, Columbia, SC
5. Eastman Kodak, Kingsport, TN
6. Hercofina, Wilmington, NC
7. Standard Oil-Amoco, Cooper River, SC
8. Standard Oil-Amoco, Decatur, Al

Fig. II-1. Locations of Plants Manufacturing Dimethyl Terephthalate and Terephthalic Acid

plant has since been sold and will be dismantled.[11] Hercofina has a captive supply of xylenes.[1]

5. Standard Oil (Indiana) (Amoco Chemicals; subsidiary)

Crude TPA is produced by oxidation of p-xylene in an acetic acid medium in the presence of a manganese acetate or cobalt acetate catalyst and an inorganic bromide.[1,8] C-TPA is purified to pure TPA (P-TPA) for the merchant market.[1] Amoco recently increased the P-TPA capacity over 50% by dedicating a new 454-Gg/yr plant at Cooper River, near Charleston, SC.[3] Amoco is also a producer of raw material p-xylene.[1] Amoco has shut down a 91-Gg/yr DMT plant at Decatur, AL, and a 68-Gg/yr DMT plant at Joliet, IL. Also, a 45-Gg/yr TPA plant in Joliet, IL, was converted to isophthalic acid production several years ago.[12]

D. REFERENCES*

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12. H. M. Brennan, Amoco Chemicals Corp., letter dated Aug. 16, 1978, to D. J. Mangum, EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC.
13. "Chemical Profile on DMT-TPA," p. 9 in Chemical Marketing Reporter (Apr. 30, 1979).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

The DMT or TPA used to make polyester must be of very high purity.[1] Crude terephthalic acid (C-TPA) that was formerly made by nitric acid oxidation of p-xylene contained impurities that were unacceptable to the polyester industry. The methanol esterification process for dimethyl terephthalate (DMT) provides a means of removing these impurities from C-TPA and produces a product of acceptable quality.[2]

C-TPA made by air oxidation of p-xylene is of higher quality than that made by nitric acid oxidation but still requires purification for use in polyester fibers. This can be done by esterification with methanol,[3] as discussed above, or by hydrogenation and crystallization from water.[1,2,4]

Another commercial route for producing DMT of polyester fiber quality is by air oxidation of a mixture of p-xylene and methyl toluate to toluic acid and monomethyl terephthalate, respectively, and subsequent methanol esterification. The methyl toluate that is formed in esterification is recycled to oxidation, and the DMT is recovered and purified by distillation.[1,2,5]

This report is primarily concerned with the air-oxidation process for C-TPA, the methanol esterification process for DMT, and the hydrogenation and crystallization process for purified terephthalic acid (P-TPA). The process for oxidation of a mixture of p-xylene and methyl toluate as practiced by Hercofina is not likely to be selected for new construction. The nitric acid oxidation process for C-TPA is no longer practiced domestically[1,6] and is not further considered in this report.

B. AIR-OXIDATION PROCESS FOR C-TPA

The model continuous process for the manufacture of C-TPA is shown in Fig. III-1. The oxidation and product recovery portion is essentially as is practiced by Amoco Chemicals, whereas the recovery and recycle of acetic acid and recovery of methyl acetate are essentially as practiced by Carolina Eastman.[3,4]

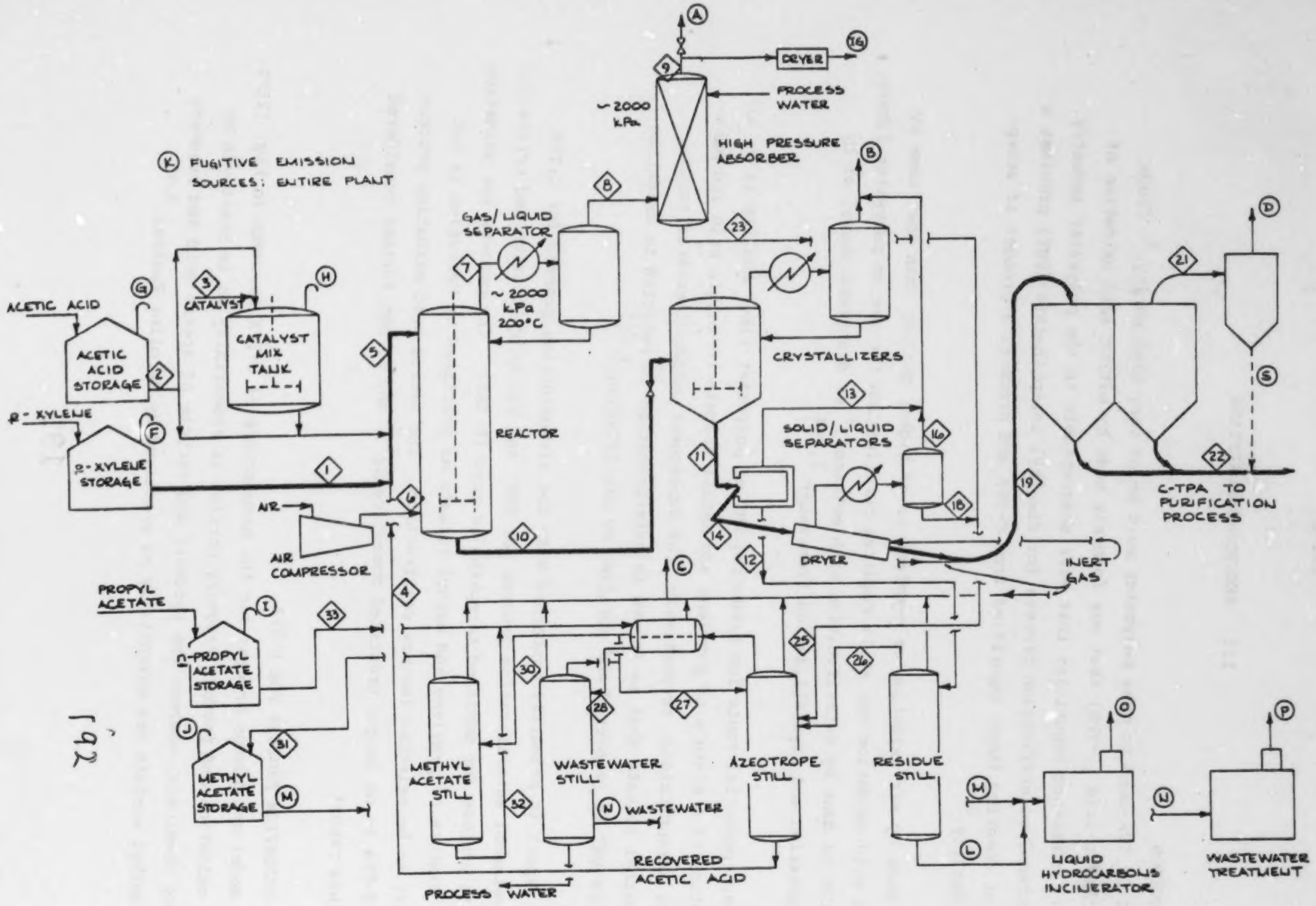
Ⓚ FUGITIVE EMISSION SOURCES: ENTIRE PLANT
ACETIC ACID
ACETIC ACID STORAGE
p-XYLENE
p-XYLENE STORAGE
CATALYST
CATALYST MIX TANK
AIR
AIR COMPRESSOR
PROPYL ACETATE
n-PROPYL ACETATE STORAGE
METHYL ACETATE STORAGE
REACTOR
GAS/LIQUID SEPARATOR
~2000 kPa 200°C
~2000 kPa
HIGH PRESSURE ABSORBER
PROCESS WATER
DRYER
CRYSTALLIZERS
SOLID/LIQUID SEPARATORS
DRYER
INERT GAS
C-TPA TO PURIFICATION PROCESS
METHYL ACETATE STILL
WASTEWATER STILL
WASTEWATER
AZEOTROPE STILL
RESIDUE STILL
RECOVERED ACETIC ACID
PROCESS WATER
LIQUID HYDROCARBONS INCINERATOR
WASTEWATER TREATMENT
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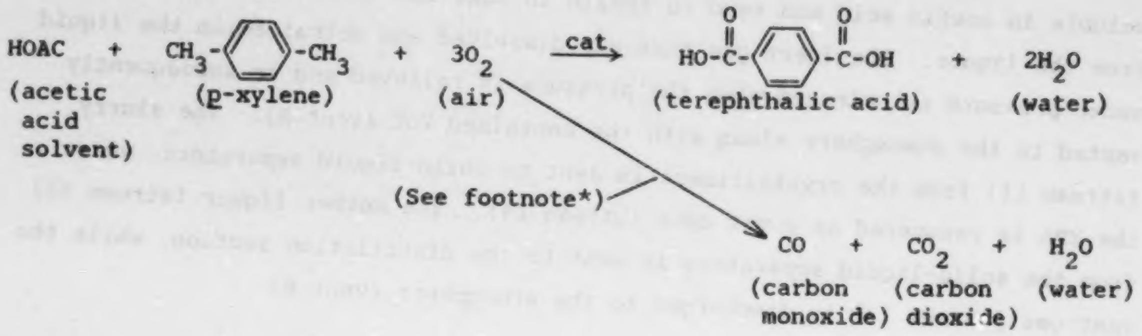
Fig. III-1. Crude Terephthalic Acid Process

1. **Chemistry**



Products of partial oxidation of p-xylene, such as p-toluic acid and p-formyl benzoic acid, are formed, with some of them appearing as impurities in TPA. Methyl acetate is also formed in significant amounts in the reaction.

2. Oxidation of p-Xylene

p-Xylene (stream 1), fresh acetic acid (stream 2), a catalyst system (stream 3), such as manganese or cobalt acetate and sodium bromide,[7] and recovered acetic acid (stream 4) are combined to comprise the liquid stream entering the reactor (stream 5). Air (stream 6), compressed to reaction pressure (about 2000 kPa), is fed to the reactor. The temperature of the exothermic reaction is maintained at about 200°C by controlling the pressure at which the reaction mixture is permitted to boil and form the vapor stream (stream 7) leaving the reactor.

Inert gases, excess oxygen, CO, CO_2, and volatile organic compounds (VOC) (stream 8) leave the gas/liquid separator and are sent to the high-pressure absorber. This stream is scrubbed with water under pressure, resulting in a gas stream (stream 9) with reduced VOC content. Part of the discharge from the high-pressure absorber is dried and is used as a source of inert gas (IG), and the remainder is passed through a pressure control valve and a noise silencer before being discharged to the atmosphere (vent A). The underflow (stream 23) from the absorber is sent to the azeotrope still for recovery of acetic acid.

3. Crystallization and Separation

The reactor liquid containing TPA (stream 10) flows to a series of crystallizers, where the pressure is relieved and the liquid is cooled by the vaporization and return of condensed VOC and water. The partially oxidized impurities are more soluble in acetic acid and tend to remain in solution while TPA crystallizes from the liquor. The inert gas that was dissolved and entrained in the liquid under pressure is released when the pressure is relieved and is subsequently vented to the atmosphere along with the contained VOC (vent B). The slurry (stream 11) from the crystallizers is sent to solid-liquid separators, where the TPA is recovered as a wet cake (stream 14). The mother liquor (stream 12) from the solid-liquid separators is sent to the distillation section, while the vent gas (stream 13) is discharged to the atmosphere (vent B).

---

*Minor reaction.

4. Drying, Handling, and Storage

The wet cake (stream 14) from solid-liquid separation is sent to dryers, where with the use of heat and IG the moisture, predominantly acetic acid, is removed, leaving the product, C-TPA, as a dry flowable solid (stream 19).

The hot, VOC-laden IG is cooled to condense and recover VOC (stream 18). The cooled IG (stream 16) is vented to the atmosphere (vent B). The condensate (stream 18) is sent to the azeotrope still for recovery of acetic acid. IG is used to convey the product (stream 19) to storage silos. The transporting gas (stream 21) is vented from the silos to dust collectors (bag-type), where its particulate loading is reduced. It is then discharged to the atmosphere (vent D). The solids (S) from the bag filter can be forwarded to purification or be disposed of by incineration.

5. Distillation and Recovery

The mother liquor (stream 12) from solid-liquid separation flows to the residue still, where acetic acid, methyl acetate, and water are recovered overhead (stream 26). The bottoms (stream L) from the still contain the products of partial oxidation, tars, catalyst residue, and some acetic acid and are sent to a liquid-waste incinerator for destruction. The overhead (stream 26) from the still and the streams (25) from the high-pressure scrubber and the product dryer are processed in the azeotrope still to remove water as an overhead stream and produce a bottoms acetic acid stream (stream 4) essentially free of water. n-Propyl acetate, used as an azeotroping agent to facilitate the separation, enters the azeotrope still through stream 27. The vapors from the still containing water, n-propyl acetate, and methyl acetate are condensed and decanted.

The aqueous phase (stream 28) is forwarded to the wastewater still, whereas the organic phase (stream 27), mainly n-propyl acetate, is returned to the azeotrope still. The aqueous phase (stream 28) contains saturation amounts of n-propyl acetate and methyl acetate, which are stripped from the aqueous phase in the wastewater still. Part of the bottoms product is used as process water in absorption and the remainder (N) is sent to wastewater treatment. A purge stream of the organic phase (stream 30) is sent to the methyl acetate still, where methyl acetate and saturation amounts of water are recovered as an overhead product (stream 31) and disposed of as a fuel (discharge M). n-Propyl acetate, obtained as the bottoms product (stream 32), is returned to the azeotrope still. A small amount of inert gas, which is used for blanketing and instrument purging, is emitted to the atmosphere (vent C). Process losses of n-propyl acetate are made up from storage (stream 33).

C. PROCESS VARIATION

In the model plant, acetic acid, used as a reaction solvent, is supplied as a raw material to replace losses of acetic acid as oxidation products and to emissions. A variation practiced by Carolina Eastman[3] is the use of acetaldehyde as a source of acetic acid for the replacements of losses. Carolina Eastman uses a somewhat different catalyst system including bromine in the form of HBr, whereas others use a bromine salt. Otherwise, the processes are very similar.

The process used by Hercofina is different from the model plant in the majority of its processing steps. Air is used for oxidation of the p-xylene as in the model plant; however, in the Hercofina process the oxidation is conducted in an excess of methyl toluate solvent, where methyl toluate is oxidized to monomethyl terephthalate. Monomethyl terephthalate, which is the main oxidation product, is esterified subsequently to DMT; terephthalic acid is not recovered as a product or intermediate in this process.

D. DMT BY ESTERIFICATION OF C-TPA

The purpose of the typical process as shown in Fig. III-2 is to convert the terephthalic acid contained in C-TPA to a form that will permit its separation from the impurities. This process is representative of current DMT technology. Terephthalic acid is converted to the dimethyl ester and is separated by fractional distillation.

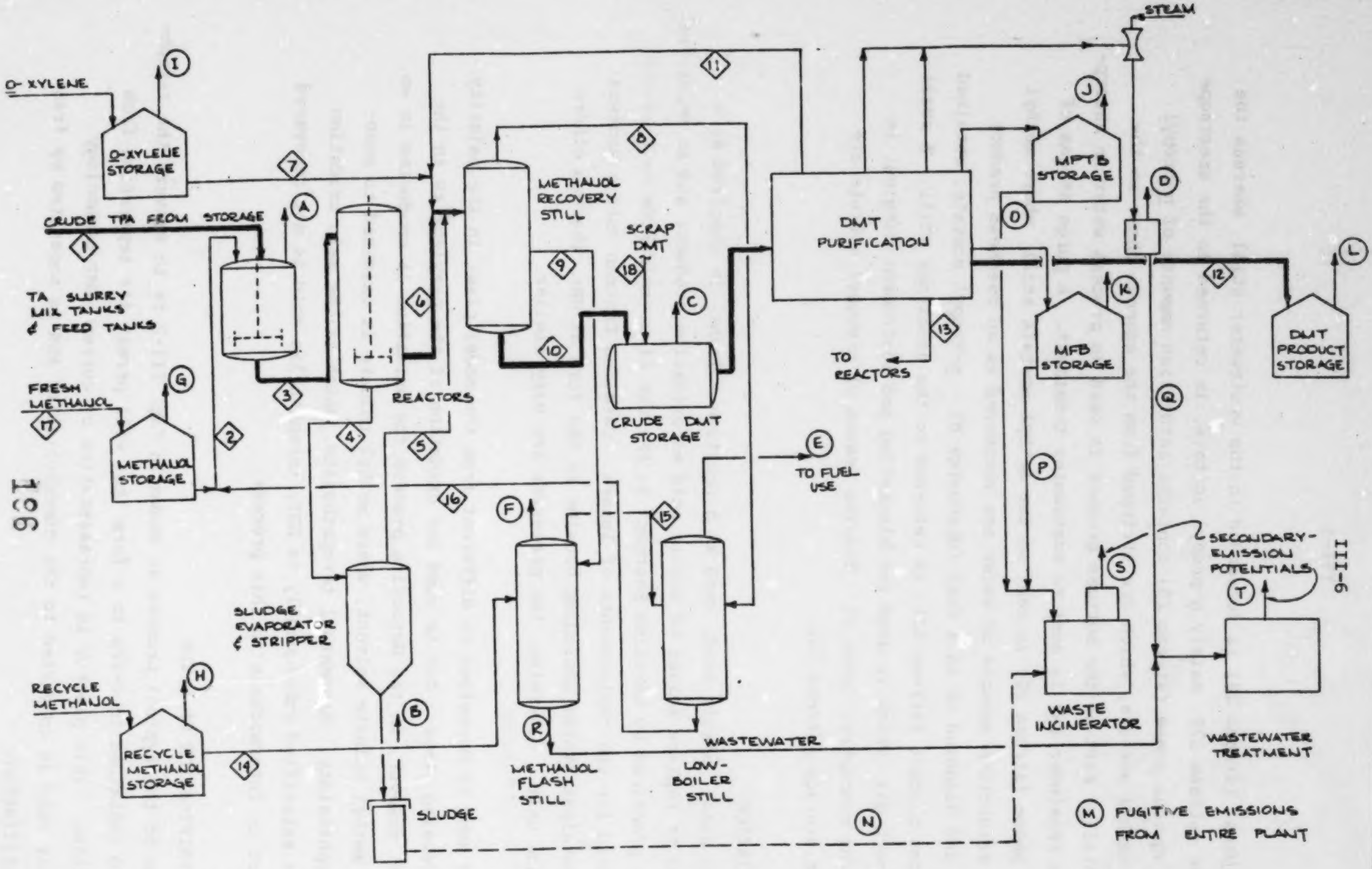

O-XYLENE
O-XYLENE STORAGE
CRUDE TPA FROM STORAGE
TA SLURRY MIX TANKS & FEED TANKS
FRESH METHANOL
METHANOL STORAGE
REACTORS
METHANOL RECOVERY STILL
SCRAP DMT
CRUDE DMT STORAGE
DMT PURIFICATION
TO REACTORS
MPTB STORAGE
MFB STORAGE
DMT PRODUCT STORAGE
STEAM
TO FUEL USE
SLUDGE EVAPORATOR & STRIPPER
RECYCLE METHANOL
RECYCLE METHANOL STORAGE
SLUDGE
METHANOL FLASH STILL
LOW-BOILER STILL
WASTEWATER
WASTE INCINERATOR
SECONDARY-EMISSION POTENTIALS
WASTEWATER TREATMENT
M FUGITIVE EMISSIONS FROM ENTIRE PLANT
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
A
B
C
D
D
E
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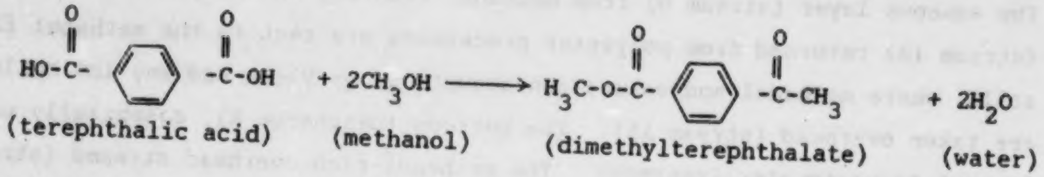
Fig. III-2. DMT by Esterification of C-TPA

1. Chemistry



2. Esterification

C-TPA (stream 1) is sent by mechanically assisted gravity feed from storage silos to slurry mix tanks, where it is mixed with methanol (stream 2) to form a slurry (stream 3) that is adequate for pumping to the continuous reactor. The esterification reaction consumes methanol and terephthalic acid and forms dimethyl terephthalate and water. A liquid purge stream (stream 4) is drawn from the reactor and is sent to the sludge evaporator and stripper for the removal and disposal of nonvolatile waste (discharge N). The volatile portion (stream 5) of the purge stream is returned to the process.

3. Methanol Recovery Still

The liquid stream (stream 6) from the reactor contains excess methanol; water, dimethyl ether, and other low boilers formed in the reactor; methyl p-toluate and methyl p-formyl benzoate that were formed in the reactor from impurities in C-TPA; and dimethyl terephthalate. Water formed in esterification is removed as the o-xylene—water azeotrope and after decantation is sent (stream 9) to the methanol flash still for recovery of the methanol that it contains. Makeup amounts of o-xylene are supplied by stream 7. Recovered methanol (stream 8), which contains lower boiling materials, is forwarded for further purification. The crude DMT (stream 10) is forwarded to DMT purification for further fractionation.

4. DMT Purification

By successive vacuum fractionation any o-xylene and light ends (stream 11) are recovered for reycle, methyl p-toluate and benzoate (MPTB) are recovered for sale or disposal as a burnable waste (discharge O), and methyl p-formyl benzoate and other materials are recovered as burnable wastes (discharge P). Finally, DMT in high purity is recovered as a finished product (stream 12) and is sent to storage. Higher boiling materials, including terephthalic acid (stream 13), are recycled to the reactor.

5. Methanol Purification

The aqueous layer (stream 9) from methanol recovery and recycled methanol (stream 14) returned from polyester processors are sent to the methanol flash still, where methanol and saturation amounts of o-xylene and any low boilers are taken overhead (stream 15). The bottoms (discharge R), essentially water, is sent to wastewater treatment. The methanol-rich overhead streams (streams 8 and 15) are sent to the low-boiler still, where dimethyl ether, other low boilers, and any noncondensable gases are removed and forwarded for use as fuel (stream E). The purified methanol (stream 16) leaves the bottom of the still and is returned to the slurry tanks, along with any fresh methanol (stream 17) needed to satisfy the methanol requirement. Scrap DMT (off-grade, etc.) is recycled (stream 18) to crude DMT storage.

E. PURIFIED TPA FROM C-TPA

The purpose of the typical process shown in Fig. III-3 is to purify C-TPA to make a terephthalic acid of quality acceptable for polyester fiber production. This is done by hydrogenation in an aqueous medium to convert the impurities, for example, p-formyl benzoic acid, to a water-soluble form such as p-toluic acid and by crystallization to yield a product [purified TPA (P-TPA)] of very high quality.[8]

1. Feed Slurry Preparation

C-TPA (stream 1) is sent by mechanically assisted gravity feed, along with hot water (stream 2), to feed slurry tanks. The gases trapped in the C-TPA granules are released to the atmosphere (vent A). The slurry of required consistency (stream 3) is sent to the dissolver, where, with the application of pressure to maintain a liquid phase, the temperature is raised to about 250°C to put the terephthalic acid in solution in the water (stream 4).

2. Reaction

Hydrogen (stream 5) in the amount of about 0.004 g per g of C-TPA, which includes a significant excess of the stoichiometric requirement, is fed to the reactor. The primary impurity, p-formyl benzoic acid, is removed by converting it to the more water-soluble p-toluic acid by the following reaction:[8]

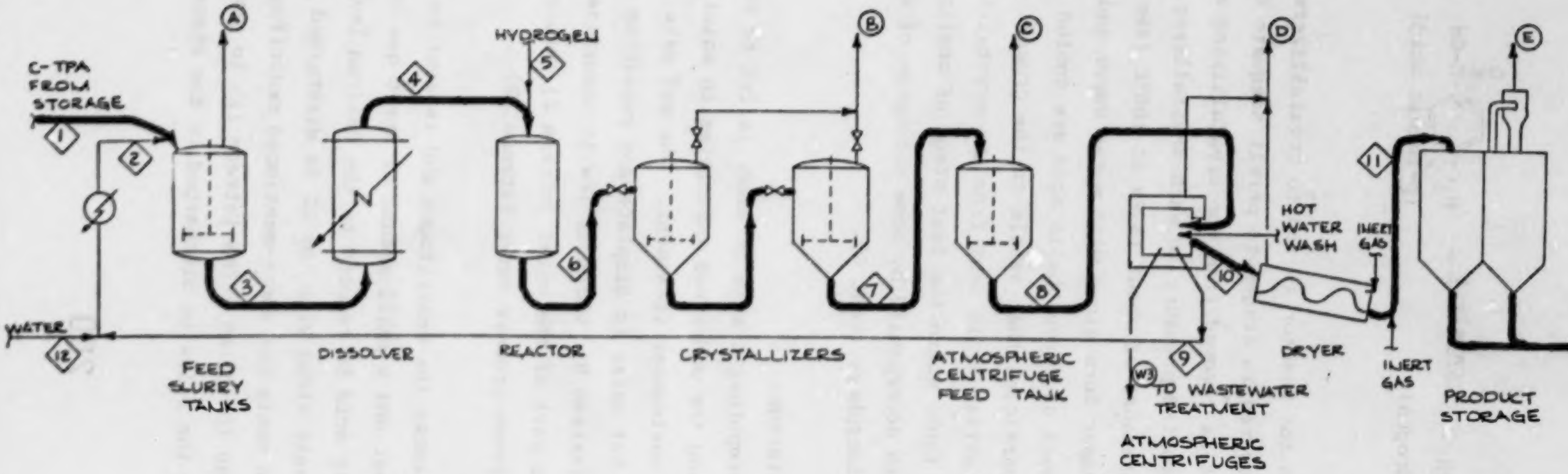
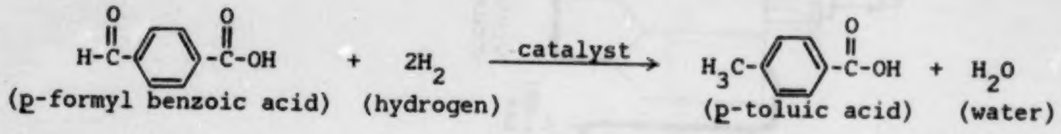

C-TPA FROM STORAGE
1
2
A
3
4
HYDROGEN
5
6
B
7
C
8
D
HOT WATER WASH
10
9
W3
TO WASTEWATER TREATMENT
INERT GAS
11
E
INERT GAS
WATER
12
FEED SLURRY TANKS
DISSOLVER
REACTOR
CRYSTALLIZERS
ATMOSPHERIC CENTRIFUGE FEED TANK
ATMOSPHERIC CENTRIFUGES
DRYER
PRODUCT STORAGE

Fig. III-3. P-TPA by Purification of C-TPA



$$H-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-OH + 2H_2 \xrightarrow{catalyst} H_3C-C_6H_4-\overset{O}{\overset{\|}{C}}-OH + H_2O$$

3. Crystallization

The discharge (stream 6) from the reactor is fed to crystallizers in series wherein the temperature is lowered in stages to permit adequate crystal growth during crystallization. Heat is removed from the crystallizing mass by allowing the water to boil under controlled pressure in each crystallizer. Since terephthalic acid exerts a vapor pressure of about 13 Pa at 100°C (see Appendix A), some TPA is emitted in the vapor form along with water vapor and the excess hydrogen (vent B). When vapors of terephthalic acid are cooled in the atmosphere, they sublime to form solid particles that settle to the ground. The slurry of terephthalic acid in water (stream 7) is sent from the crystallizers to the atmospheric centrifuge feed tank, where the last stage of cooling and crystallization occurs. This is again accompanied by some discharge of water and terephthalic acid vapors to the atmosphere (vent C).

4. Centrifuging, Drying, and Storage

The slurry (stream 8) of terephthalic acid in water is fed to centrifuges, where the mother liquor, containing the undesired impurities in solution, is removed (discharge W3) and sent to wastewater treatment. The wet cake, still in the centrifuge, is washed with hot water to displace any remaining mother liquor. The resultant wash liquor (stream 9), which is low in impurities, is forwarded to the feed slurry tanks as part of the water (stream 2) required in the reactor; the balance is made up by fresh process water (stream 12).

The wet cake (stream 10) leaves the centrifuges and is sent to the dryer, where with the application of heat and a small amount of inert gas (IG) the moisture content of the terephthalic acid is reduced to the desired level. The moisture that is removed from the cake along with the IG is discharged to the atmosphere through a header that also vents the above-mentioned centrifuges (vent D). Inert gas is used to convey the dried P-TPA (stream 11) to product storage. The transport gas leaving the silos is discharged to the atmosphere (vent E).

F. REFERENCES*

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2. B. V. Vora et al., "The Technology and Economics of Polyester Intermediates," Chemical Engineering Progress 73(8), 74—80 (August 1977).

3. S. W. Dylewski, IT Enviroscience, Inc., Trip Report for Visit to Carolina Eastman Company, Columbia, SC, Dec. 6, 7, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

4. S. W. Dylewski, IT Enviroscience, Inc., Trip Report for Visit to Amoco Chemicals Corporation, Decatur, AL, Oct. 31, Nov. 1, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

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7. L. M. Elkin, "Terephthalic Acid and Dimethyl Terephthalate," pp. 49—55 in Report No. 9, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (February 1966).

8. AMOCO, Standard Oil Co. (Indiana), Terephthalic Acid and Purified Terephthalic Acid Processes [16-105-P(1-75)] (unpublished report).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

Process emissions from the model plants are based on emission data included in trip reports, responses to EPA letters requesting information from sites not visited, and the GCA technology reports.[1—7] Literature sources, such as the SRI Chemical Economics Handbook and the Kirk-Othmer Encyclopedia of Chemical Technology, were utilized to gain a better understanding of process unit operations and process chemistry.

A. CRUDE TEREPHTHALIC ACID PROCESS

1. Model Plant*

The model plant (Fig. III-1) has a crude terephthalic acid (C-TPA) capacity of 230 Gg/yr based on operating 8760 hr/yr.** A number of existing production units are of this size, but the older units are smaller.

Typical raw-material, in-process, product, and waste by-product storage-tank capacities are estimated for the 230-Gg/yr plant. The storage-tank parameters are given in Sect. IV.A.2.e, and estimates of potential fugitive emission sources are given in Sect. IV.A.2.f. Characteristics of the model plant that are important in air-dispersion modeling are given in Table B-1 in Appendix B.

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*See p. I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

2. Sources and Emissions

Emission sources and quantities for the C-TPA process are summarized in Table IV-1.

a. Reactor Vent—The reactor vent gas (A, Fig. III-1) contains nitrogen (from air oxidation); unreacted oxygen; unreacted p-xylene; acetic acid (reaction solvent); carbon monoxide, carbon dioxide, and methyl acetate resulting from oxidation of p-xylene and acetic acid that are not recovered by the high-pressure absorber; and water, some of which results from oxidation and some from evaporation during absorption with water in the high-pressure absorber. Table IV-2 gives the composition of this stream based on consideration of data from several sources.[3,4,7,8] The quantity of VOC emitted at vent A can be higher if the absorber is operated at a lower pressure than that in the model plant. The quantity can also vary with the temperature of the exiting vent gases.

b. Crystallization, Separation, and Drying Vent—The gases vented from the crystallization of terephthalic acid and the separation of the crystallized solids from the solvent by centrifugation or by filtration are the noncondensable gases that are released during crystallization and the VOC vapors that are carried by those gases. These vent gases and the C-TPA dryer vent gas are combined and released to the atmosphere (B, Fig. III-1). Different methods employed in this processing section can result in less noncondensable gases and less accompanying VOC being emitted from this vent. However, the VOC emission from the reactor vent may be commensurately increased.[3,4,7,8]

c. Distillation and Recovery Vent (C, Fig. III-1)—The gases vented from the distillation section are the small amount of gases dissolved in the feed stream to distillation, the inert gas used in inert blanketing, in instrument purging, and in pressure control, and the VOC vapors that are carried by the noncondensable gases. The quantity of this discharge is normally small.[3,4,7,8]

d. Product Transfer Vent—The gas vented (D Fig. III-1) from the bag filters on the product storage tanks (silos) is dry, reaction-generated, inert gas containing the VOC that were not absorbed in the high-pressure absorber. The vented gas stream contains a small quantity of TPA particulate that is not removed by the bag filters.[3,4,7]

Table IV-1. Uncontrolled VOC Emissions from Crude Terephthalic Acid Model Plant

Emission Source	Stream Designation (Fig.III-1)	Emissions Ratio (g/kg)[a] VOC	Emissions Ratio (g/kg)[a] CO	Emissions Rate (kg/hr)[b] VOC	Emissions Rate (kg/hr)[b] CO
Reactor vent	A	14.6	17	383.3	446
Crystallization, separation, and drying vent	B	1.9		49.9	
Distillation and recovery vent	C	1.14		29.9	
Product transfer vent[c]	D	1.78[d]	2	46.7[d]	53
Storage and handling					
Raw material storage	F,G,I	0.112		2.94	
Other storage	H,J	0.006		0.17	
Fugitive	K	0.58		15.26	
Secondary					
Incinerator	L	0.00482		0.126	
	M	0.00123		0.0323	
Wastewater treatment	N	<0.004	—	<0.1	—
Total		20.13	19	528.4	499

[a] g of emission per kg of product produced.

[b] Based on 8760 hr of operation per year.

[c] Stream contains 0.7 g of TPA particulates/kg; not included.

[d] VOC and CO emissions originated in reactor off-gas used for transfer.

Table IV-2. Composition of Model-Plant Reactor Vent Gas (Vent A)[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Nitrogen	94.71	1985
Oxygen	2.58	54
CO_2	0.91	19
CO	0.81	17
p-Xylene	0.29	6
Acetic acid	0.03	0.6
Methyl acetate	0.38	8
Water	0.29	6
	100.00	2095.6

[a] See refs 3, 4, 7, and 8.

[b] g of emission per kg of C-TPA produced.

e. Storage and Handling Emissions——Emissions result from storage of p-xylene, acetic acid, and n-propyl acetate. The emission from p-xylene storage occurs only during filling of the tanks since they are maintained at a constant temperature. Sources for the model plant are shown in Fig. III-1 (F through J). Storage-tank parameters for the model plant are given in Table IV-3. The calculated emissions in Table IV-1 are based on fixed-roof tanks, half full, an 11°C diurnal temperature variation, and the use of the emission equations from AP-42.[9] However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overestimates emissions.

There are no VOC handling emissions since the product, C-TPA, is transferred in the solid form and by-product waste methyl acetate is transported by pipeline to incinerators.

f. Fugitive Emissions——Pumps, compressors, valves, and pressure relief devices on VOC-containing streams are potential sources of fugitive emissions (K in Fig. III-1). The model plant is estimated to have 50 pumps, 900 process valves, and 40 pressure relief devices in VOC service. The fugitive emission factors from Appendix C were applied to these estimates, and the totals are shown in Table IV-1.

g. Secondary Emissions——Secondary emissions can result from the handling and disposal of process waste-liquid streams. Three potential sources (L, M, and N) are indicated in Fig. III-1 for the model plant. The secondary emissions from burning still residues (L) and methyl acetate waste (M) were calculated with the emission factors from AP-42 for residue oil and distillate oil, respectively.[10] The still residues also contain some bromine compounds and inorganic solids. Care must be exercised upon incineration to avoid the release of free bromine and particulates to the atmosphere.

The secondary emissions from wastewater treatment (source P) were estimated by procedures that are discussed in a separate EPA report on secondary emissions. An estmate of wastewater composition and flow rate was made, based on industry data.[4] A Henry's-law constant was then calculated for the vapor-liquid system and the emission rate was estimated by the estimating approaches given in the literature.[11,12]

Table IV-3. Crude Terephthalic Acid Model-Plant Storage-Tank Data

Purpose	Content	Quantity	Size (m^3)	Turnovers/yr	Temperature (°C)[a]
Raw material	p-Xylene	2	5770	15.9	42[b]
In-process	p-Xylene	1	1000	2[c]	42[b]
Raw material	Acetic acid	1	660	15.9	25
Mother liquor	Acetic acid	1	1200	2[c]	40
Raw material	Propyl acetate	1	114	12	25
Catalyst mix	Acetic acid	1	455	2[c]	40
Burner feed	Methyl acetate	1	114	2[c]	25
Product	C-TPA	4	4600	21	25

[a] Average bulk temperature.

[b] Controlled temperature.

[c] These tanks operate at essentially constant level, and the turnovers represent shutdown events.

B. C-TPA PROCESS VARIATION

In the Carolina Eastman process, where acetaldehyde is used to make up acetic acid losses, the VOC emissions are very similar to those associated with the model process with the exception that in the acetaldehyde process a small amount of methyl bromide is also emitted.[4]

A discussion regarding the Hercofina process is presented in Sect. IV-D.

C. DMT BY ESTERIFICATION OF C-TPA

1. Typical Plant

The typical plant (Fig. III-2) for dimethyl terephthalate (DMT) production has a capacity of 269 Gg/yr (1.17 X C-TPA capacity) based on operating 8760 hr/yr. Some existing production units are of this size;[4] other units are smaller.[7,13] New construction will likely be of the capacity of the typical plant.

2. Sources and Emissions

Uncontrolled VOC emission quantities from process, storage, fugitive, and secondary sources in DMT production are summarized in Table IV-4 and are discussed below. The discharge locations are shown in Fig. III-2.

a. Slurry Mix Tank Vent——The gases present in the voids of the crude terephthalic acid (C-TPA) bulk solid are displaced by and saturated with methanol during slurry preparation. The gas/vapor mixture is released at vent A.[4—6]

b. Reactor Sludge Transfer Vent——Some of the impurities and the catalyst contained in C-TPA are discharged from the crude reaction stream after evaporation and stripping of the catalyst. This discharge is accompanied by some DMT particulate emission at vent B.[4—6]

c. Vacuum Jet Condenser Vent——Air in-leakages occurring during vacuum distillation, along with some VOC, are discharged at vent D.[4—6]

d. Methanol Flash Still Vent——Inert gases that originate in recycled methanol (returned from polymer plant) and that are introduced for blanketting, along with some VOC, are discharged at vent F.[4—6]

Table IV-4. Uncontrolled VOC Emissions from Typical Dimethyl Terephthalate Plant

Emission Source	Stream Designation (Fig.III-2)	Emissions Ratio[a] (g/kg)	Emissions Rate[b] (kg/hr)
Slurry mix tank vent	A	1.0	30.72
Reactor sludge transfer vent	B	c	c
Vacuum jet condenser vent	D	0.34	10.44
Methanol flash still vent	F	0.02	0.61
Storage vents			
Crude DMT	C	0.09	2.80
Methanol	G,H	0.13	3.99
DMT	L	e	e
Other storage	I—K	0.03	0.92
Fugitive	M	0.66	20.43
Secondary			
Process boiler	E	0.0018	0.06
Incinerator	N—P	NS[d]	NS
Wastewater	Q,R	NS	NS
		2.27	69.9

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[a] g of emission per kg of product.

[b] Based on 8760 hr of operation per year.

[c] Particulate emission of 0.038 g/kg and 1.17 kg/hr.

[d] Not significant.

[e] Particulate emission of 0.18 g/kg and 5.53 kg/hr.

e. Storage and Handling Emissions---Emissions result from storage of recycled and fresh methanol, from o-xylene, and from certain in-process tanks containing VOC. Location of storage tank vents C, G—L are shown in Fig. III-2. The quantities shown in Table IV-4 are representative of the emissions reported by industry.[4—6]

f. Fugitive Emissions---Pumps, compressors, process valves, and pressure relief devices on VOC-containing streams are potential sources of fugitive emissions (M, Fig. III-2). The typical DMT plant is estimated to have 89 pumps, 1100 process valves, and 16 pressure relief devices. The fugitive emission factors from Appendix C were applied to these estimates, and the totals are shown in Table IV-4.

g. Secondary Emissions---Emissions can result from the handling and disposal of gaseous and liquid process wastes. Stream E, containing dimethyl ether and other vapors, is sent by pipeline to a process boiler, where it is used as a fuel. The emission from this source is very small,[10] as are the emissions from incineration of waste streams N, O, and P. The wastewater streams (Q,R) going to wastewater treatment are small and the emission from their disposal is also expected to be small.

D. PROCESS VARIATION

In the process used by Hercofina, where air is used to oxidize a mixture of p-xylene and methyl p-toluate, the light ends that are formed and the p-xylene that does not react are carried on a stream of nitrogen and other gases. The uncontrolled VOC from the oxidation reactor can be as much as 124 g/kg of DMT and from the esterification can be 68 g/kg of DMT; other emissions from this process are similar to those for the typical plant for production of DMT.[14]

E. PURIFIED TPA FROM C-TPA

The purification of C-TPA by hydrogenation in an aqueous medium does not involve the handling or generation of VOC; therefore no VOC are emitted to the atmosphere. During the venting of excess hydrogen and water vapor at elevated temperatures, vaporized TPA is emitted; however, the TPA vapors sublime on contact with the atmosphere and fall to the ground. Since this emission is not considered to be VOC, no further treatment of this process will be addressed. The particulate emissions for P-TPA of 230-Gg/yr capacity are shown in Table IV-5.[3,7]

Table IV-5. Emission from Purified Terephthalic Acid Typical Plant[a]

Emission Source	Stream Designation (Fig.III-3)	Emissions[b] Ratio[c] (g/kg)	Emissions[b] Rate[d] (kg/hr)
Feed slurry tank vent	A	0.088	5.08[e]
Crystallizer vent	B	0.098	5.69[e]
Atmospheric centrifuge feed tank	C	0.023	1.32[e]
Dryer vent	D	0.0012	0.07[e]
Silo dust collector vent	E	0.0017	0.10

[a] See ref 7.

[b] Emissions shown are TPA particulates. No VOC present in processing steps.

[c] g of emission per kg of product.

[d] Based on 8760-hr/yr operation.

[e] Emission quantities following water scrubber.

F. REFERENCES*

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. CRUDE TEREPHTHALIC ACID PROCESS

1. Reactor Vent and Product Transfer Vent

There is demonstrated performance of carbon adsorption of VOC from a gas stream similar to the reactor vent gas and product transfer vent gas (A and D, respectively, Fig. III-1).[1] It is estimated that the vent stream from the model plant will perform similarly in carbon adsorption and effect a VOC emission reduction of 97% or greater. It should be noted that the CO emissions will not be reduced by carbon adsorption.

The reactor vent gas passes through one of the carbon beds, where the VOC are adsorbed, and is then released to the atmosphere. When the first carbon bed approaches breakthrough, the feed gas is routed to another carbon bed. At this point regeneration of the first bed by steam stripping is started. The VOC-laden stripping steam is then condensed and decanted. The *p*-xylene layer is returned to the reactor section, and the aqueous layer is forwarded to distillation for recovery of the water-soluble VOC. When essentially all the VOC are stripped from the first bed, a purge stream of VOC-depleted effluent from the second bed is forced by a blower through the first bed to purge the remaining VOC and to cool the bed for adsorption.

An alternative to the carbon adsorption system employed in the controlled model plant is a thermal oxidizer. With a properly designed system operating at 1100°C for efficient CO destruction, a reduction of 99% or greater in VOC and in CO can be achieved. Because of the high percentage of nitrogen present in the vent gas, 176 GJ of supplemental fuel per hour is needed to achieve the desired temperature. Although 133 GJ/hr of energy as steam can be recovered, the energy requirement balance of the plant needs to be considered. Thermal oxidation is covered by a separate EPA report.[2]

A reduction in emissions from vents A and D can be achieved by a change in the high-pressure absorber in the model plant by providing a compound system rather than the usual multistage system wherein the liquor from the lower portion is largely recycled and the upper portion is irrigated by once-through water, as is practiced by Carolina Eastman.[3] This modification could reduce VOC emissions from vents A and D by 36%.

2. Crystallization, Separation, and Drying Vent and Distillation and Recovery Vent

The emissions from the crystallization, separation, and drying vent (B, Fig. III-1) and from the distillation and recovery vent (C, Fig. III-1) can be piped to a header; the combined streams can be controlled by compressing the vent gas with a blower, combining it with stream 9 (Fig. III-1), and sending the combined stream to the carbon adsorption system. The VOC emission reduction is estimated to be 97% or greater (B, C, Table V-1).

An alternative to the carbon adsorber for vent streams B and C is the use of aqueous absorbers. The absorption of acetic acid from stream B will reduce emissions by 98%,[4] and the absorption of methyl acetate from stream C will reduce emissions by 96%.[3]

3. Storage and Handling Emissions

The emissions from p-xylene storage tanks (F, Fig. III-1) are not large at the storage temperature of 42°C and a vapor pressure of 3 kPa; therefore no controls are indicated. The industry does, however, use conservation vents to minimize losses. The emissions from acetic acid storage tanks (G, H, Fig. III-1) are controlled by being vented through aqueous absorbers, as is done in industry.[4,5] The resultant aqueous solution is returned to the process. The emissions from methyl acetate storage (J) are also controlled by an aqueous absorber. An alternative to the use of an aqueous absorber is to collect, compress, and send the emissions from vents G, H, and J to the above carbon adsorber. Handling of the product, a solid with a high melting point (see Appendix A), does not result in VOC emissions. Options for control of storage and handling emissions are covered in a separate EPA report.[6]

4. Fugitive Emissions

Controls for fugitive emissions from the synthetic organic chemical manufacturing industry are discussed in a separate EPA document.[7] Controlled fugitive emissions (K) calculated with factors given in Appendix C are included in Table V-1; these factors are based on the assumption that major leaks are detected by an appropriate leak-detection system and corrected.

Table V-1. Controlled Emissions from Crude Terephthalic Acid Model Plant[a]

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions Ratio (g/kg)[b] VOC	Emissions Ratio (g/kg)[b] CO	Emissions Rate (kg/hr) VOC	Emissions Rate (kg/hr) CO
Reactor vent	A	Carbon adsorber	97+	0.44	17	11.5	446
Crystallization, separation, and drying vent	B	Carbon adsorber	97+	0.057		1.50	
Distillation and recovery vent	C	Carbon adsorber	97+	0.034		0.89	
Product transfer vent[c,d]	D	Carbon adsorber	97+	0.053	2	1.41	53
Storage vents							
p-Xylene	F	None		0.11		2.81	
Acetic acid and methyl acetate	G,H,J	Aqueous absorber	98	0.0001		0.003	
Propyl acetate	I	None		0.001		0.036	
Fugitive	K	Detection and correction of major leaks	71	0.169		4.42	
Secondary							
Incineration	L,M	None		0.006		0.158	
Wastewater treatment	N	None		<0.004	—	<0.100	—
				0.874	19	22.8	499

[a] All emissions are based on 8760 hr of operation per year.

[b] g of emission per kg of product.

[c] VOC and CO emissions originated in reactor off-gas used for transfer.

[d] Stream also contains 0.7 g of TPA particulates/kg; not included.

5. Secondary Emissions

Secondary VOC emissions resulting from burning the still residues and methyl acetate waste (L and M, respectively, Fig. III-1) are estimated to be very small. No control has been identified for the model plant. Still residues (L) containing bromine and inorganic solids will probably require either prior removal or post-incineration emission-control devices to control bromine and particulate emissions to the atmosphere. Calculations based on estimated wastewater flow rates and compositions for the model plant indicate that the emissions from wastewater treatment of these wastes are relatively small. No control system has been identified for the model plant.

B. C-TPA PROCESS VARIATION

In the Carolina Eastman process, where acetaldehyde is used to make up acetic acid losses, a small amount of methyl bromide is present in the emissions and it is not certain how stable this chemical is in carbon adsorption nor how effectively it can be removed and recovered.

C. CURRENT EMISSION CONTROL USED IN C-TPA PRODUCTION

The control devices and techniques in current use by the terephthalic acid producers are discussed in Appendix E.

D. DMT BY ESTERIFICATION OF C-TPA

1. Slurry Mix Tank Vent

The VOC emission from the slurry mix tank vent (A, Fig. III-2) can be controlled by passing the vent gas through an *o*-xylene absorber. *o*-Xylene has a higher boiling point than methanol and is a solvent for methanol (see Appendix A). Based on industry experience[5] and supported by engineering data, the VOC emission reduction is estimated to be 96% or greater (A, Table V-2).

2. Reactor Sludge Transfer Vent

The DMT particulate emission from the reactor sludge transfer vent (B, Fig. III-2) can be essentially completely controlled by an *o*-xylene absorber; however, some VOC emission is created by the vaporization of *o*-xylene into the carrier gas (B, Table V-2).

Table V-2. Controlled VOC Emissions from Dimethyl Terephthalate Typical Plant

Emission Source	Stream Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	VOC Emissions	
				Ratio (g/kg)^{a}	Rate (kg/hr)^{b}
Slurry mix tank vent	A	o-Xylene absorber	96	0.04	1.23
Reactor sludge transfer vent	B	o-Xylene scrubber	c	0.011^{d}	0.34^{d}
Vacuum jet condenser vent	D	Refrigerated condenser	81	0.065	1.98
Methanol flash still vent	F	None		0.02	0.61
Storage vents					
Crude DMT	C	o-Xylene absorber	99	0.0009	0.028
Methanol	G,H	Water absorber	90	0.013	0.40
DMT	L	Methanol scrubber	c	0.19^{e}	5.84
Other storage	I—K	Conservation vent		0.03	0.92
Fugitive	M	Detection and correction of major leaks	73	0.175	5.45
Secondary	E	None		0.0018	0.06
	N—P	None		NS^{f}	NS
	Q,R	None		NS	NS
				0.54	16.8

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[a] g of emission per kg of product.

[b] Based on 8760 hr of operation per year.

[c] Particulate reduction is essentially 100%.

[d] Some o-xylene is vaporized.

[e] Methanol vaporized during scrubbing.

[f] Not significant.

3. Vacuum-Jet Condenser Vent

The VOC emission from the vacuum-jet condenser vent (D, Fig. III-2) is mainly o-xylene, which can be reduced by 81% with the use of a refrigerated condenser (D, Table V-2).

4. Methanol Flash-Still Vent

No control has been indicated for this source (F, Table V-2). The gases from this vent can be controlled by combining it with vent A, which is controlled by an o-xylene absorber.

5. Storage Emissions

Emission of VOC from crude DMT storage, at an elevated temperature, is controlled by an o-xylene absorber and results in a reduction of 99% or greater (C, Table V-2).

Methanol storage vents are controlled by a water absorber and results in a reduction of 90% or greater (G and H, Table V-2).

The particulate emisson from DMT storage is essentially completely controlled by a methanol scrubber. There is, however, some vaporization of methanol into the carrier gas (L, Fig. III-2). If o-xylene were considered by industry to be a feasible medium for scrubbing DMT particulate, with a lower vapor pressure less vapors would be emitted with the carrier gas. The remaining storage tanks with minor emissions are equippped with conservation vents but are otherwise uncontrolled (I-K, Fig. III-2). Options for control of storage emissions are covered in a recent EPA report.[6]

6. Fugitive Emissions

Controls for fugitive emissions from the synthetic organic chemical manufacturing industry are discussed in a separate EPA document.[7] Controlled fugitive emissions calculated with factors given in Appendix C are included in Table V-1; these factors are based on the assumption that major leaks are detected by an appropriate leak-detection system and corrected.

7. Secondary Emissions

No controls are identified for emissions occurring when discharges E, N—P (Fig. III-2) are burned. No controls are identified for emission from wastewater treatment of discharges Q and R (Fig. III-2).

E. CURRENT EMISSION CONTROL USED IN DMT PRODUCTION

The control devices and techniques in current use by the dimethyl terephthalate acid producers are discussed in Appendix E.

F. DMT PROCESS VARIATION

In the process used by Hercofina, where air is used to oxidize a mixture of *p*-xylene and methyl *p*-toluate, an aqueous absorber is used to control the emission of methanol and low boilers that are carried by inert gases from methanol recovery. About 99% of the methanol emission is reduced. No data are available on reduction of low-boiler emissions.[1]

G. PURIFIED TPA FROM C-TPA

Water scrubbers are used to control the particulate emissions from the purified TPA process.[4]

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5. D. W. Smith, E. I. du Pont de Nemours and Co., letter dated Oct. 20, 1978, in response to EPA's request for information on emissions from TPA/DMT production facilities.

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7. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

8. D. F. Durocher et al., p. 4 in Screening Study to Determine Need for Standards of Performance for New Sources of Dimethyl Terephthalate and Terephthalic Acid Manufacturing, EPA Contract No. 68-02-1316, Task Order No. 18 (July 1976).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Crude Terephthalic Acid Model Process

Table VI-1 shows the environmental impact of reducing the VOC emissions by application of the indicated controls to the several sources from the model plant. The total reduction is indicated to be 4429 Mg/yr for the model plant.

a. Process Vents—The carbon adsorber used for control of emissions from the reactor vent (A), the crystallization, separation, and drying vent (B), the distillation and recovery vent (C), and the product transfer vent (D) reduces the VOC emissions by 4333 Mg/yr. The carbon adsorber uses steam and cooling water during regeneration and power for the blowers, instruments, and lighting. The aqueous stream containing VOC that is recovered requires additional steam and cooling water in the recovery steps. The total energy required in the form of steam and power to recover the VOC as indicated is 16 GJ/hr.

b. Other Emissions (Storage, Fugitive, and Secondary)—Control methods described for these sources for the model plant are aqueous absorbers for some storage vents and correction of leaks for fugitive emissions. Application of these systems results in a VOC emission reduction of 96 Mg/yr for the model plant.

The electrical energy and the process water required for the aqueous absorber are negligible.

2. C-TPA Process Variations

The environmental and energy impacts of controlling the emissions from processes using acetaldehyde to make up acetic acid losses are similar to the impacts described for the model plant except for the possible need for a small amount of caustic to neutralize by-products of methyl bromide hydrolysis.

3. 1979 C-TPA Industry Emissions

The total VOC emissions from process, storage, fugitive, and secondary sources during the domestic production of crude terephthalic acid in 1979 are estimated to be 28.6 Gg. This is based on an estimated 1979 level of production of 1655 Gg

Table VI-1. Environmental Impact of Controlled Crude Terephthalic Acid Model Plant

Emission Source	Vent Designation (Fig. III-1)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)*
Reactor vent	A	Carbon adsorber	97	3257
Crystallization, separation, and drying vent	B	Carbon adsorber	97	423
Distillation and recovery vent	C	Carbon adsorber	97	255
Product transfer vent	D	Carbon adsorber	97	398
Storage	F,I	None		
	G,H,J	Aqueous absorber	98	1
Fugitive	K	Detection and correction of major leaks	71	95
Secondary	L,M,N	None		
Total				4429

*Basis is 8760 hr of operation per year.

of C-TPA required to produce the P-TPA and DMT (Hercofina not included). The demand for these products is calculated by applying the estimated 7.75% annual growth rate to the reported production for 1978 (see Sect. II),[1] the estimated emission ratios (see Tables IV-1 and V-1), and the level of control practiced in the industry (see Table E-1). The process emissions are estimated to be 14% controlled, storage emissions to be 5% controlled, fugitive emissions to be 50% controlled, and secondary sources to be uncontrolled.

4. DMT by Typical Process for Esterification of C-TPA

Table VI-2 shows the environmental impact of reducing the VOC emissions by application of the indicated controls to the several sources from the typical plant. The total reduction is indicated to be 465 Mg/yr for the typical plant.

a. Process Vents——The *o*-xylene absorbers used for control of emissions from the slurry mix tank vent (A), the reactor sludge transfer vent (B), and the refrigerated condenser used for control of emissions from the vacuum-jet condenser vent (D) reduce the VOC emissions by 330 Mg/yr. The energy impact of these emission control devices will not be significant.

b. Other Emissions (Storage, Fugitive, and Secondary)——Control methods described for these sources for the typical plant are an *o*-xylene absorber for crude DMT storage, a water absorber for methanol storage, and a methanol scrubber for control of particulates from DMT storage. Control of fugitive emissions is by adequate methods of leak detection and maintenance. Application of these systems results in a VOC emission reduction of 136 Mg/yr.

5. 1979 Industry Emissions from DMT via C-TPA (70% of DMT Production)

The total VOC emissions from process, storage, fugitive, and secondary sources from the production of DMT from C-TPA domestically in 1979 are estimated to be 1.26 Gg. This is based on an estimated 1979 level of production of 926 Gg, which is calculated by applying the estimated 7.75% annual growth rate to the reported production for 1978 (see Sect. II),[1] the estimated emission ratios (see Tables IV-4, V-2), and the level of control practiced in the industry (see Table E-2). The process emissions are estimated to be 49% controlled, storage emissions to be 28% controlled, fugitive emissions to be 50% controlled, and secondary sources to be uncontrolled.

Table VI-2. Environmental Impact of Controlled Dimethyl Terephthalate Typical Plant

Emission Source	Vent Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction	
			(%)	(Mg/yr)[a]
Slurry mix tank vent	A	o-Xylene absorber	96	258.33
Reactor sludge transfer vent[b]	B	o-Xylene scrubber		(2.98)[c]
Vacuum jet condenser vent	D	Refrigerated condenser	81	74.11
Methanol flash still vent	F	None		
Storage vents				
Crude DMT	C	o-Xylene absorber	99	24.28
Methanol	G,H	Water absorber	90	31.45
DMT[b]	L	Methanol scrubber		(51.16)[d]
Other storage	I—K	None		
Fugitive	M	Detection and correction of major leaks	73	131
Secondary	E, N—P, Q, R	None		
				465.03

[a] Basis is 8760 hr of operation per year.

[b] DMT particulate emitted.

[c] Vaporized o-xylene emitted.

[d] Vaporized methanol emitted.

6. 1979 Industry Emissions from DMT via Hercofina Process (30% of DMT Production)
The total VOC emissions from process sources from the production of DMT via the Hercofina process[1] in 1979 are estimated to be 6.0 Gg. This is based on an estimated 1979 level of production of 394 Gg, which is the same percent of capacity operation as the estimate for the entire industry.

B. CONTROL COST IMPACT

1. Crude Terephthalic Acid Process

This section gives estimated costs and cost-effectiveness data for control of VOC emissions from crude terephthalic acid production. Details of the model plant (Fig. III-1) are given in Sects. III and IV. Cost estimates were determined by using the control device evaluation report for carbon adsorption.[2] The procedure used is described in Appendix D.

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of crude terephthalic acid production lost during installation or startup, research and development, or land acquisition.

The bases for the annual cost estimates for the control alternatives include utilities, waste disposal, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-3. Recovery credits are based on the raw-material value or the fuel value of the materials being recovered. Annual costs are end-of-year costs for 1979.

a. Process Vents——The estimated installed capital cost of a carbon adsorption system designed to reduce the VOC emissions from the process vents by 97% or greater is $1,100,000 (see Appendix D).

The process-vent gas rate varies directly with the production rate; Fig. VI-1 was plotted to show the variation of installed capital cost of a carbon adsorption system versus plant capacity.

Table VI-3. Factors Used in Computing Annual Costs

Carbon loading	15 kg VOC/100 kg carbon
Steam for regeneration	0.6 kg/kg of carbon
Granular activated carbon replacement every 5 yr	\$2.57/kg[a]
Utilities	
Steam	\$2.37/GJ (\$2.50/10^3 lb)
Electricity	\$8.33/GJ (\$0.03/kWh)
Cooling water	\$0.026/m^3 (\$0.10/10^3 gal)
Fixed costs	
Maintenance labor plus materials, 6%	29% installed capital
Capital recovery, 18% (10 yr life @ 12% interest)	
Taxes, insurance, administration charges, 5%	
Recovery credits	
Acetic acid	\$0.42/kg[b]
p-Xylene	\$0.44/kg[b]
Methyl acetate	\$0.0083/kg[c]

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[a] If it became necessary to replace the carbon every 2 yr, the cost would increase \$24,314/yr.

[b] See ref 3.

[c] Based on fuel equivalent value of \$1.90/GJ.

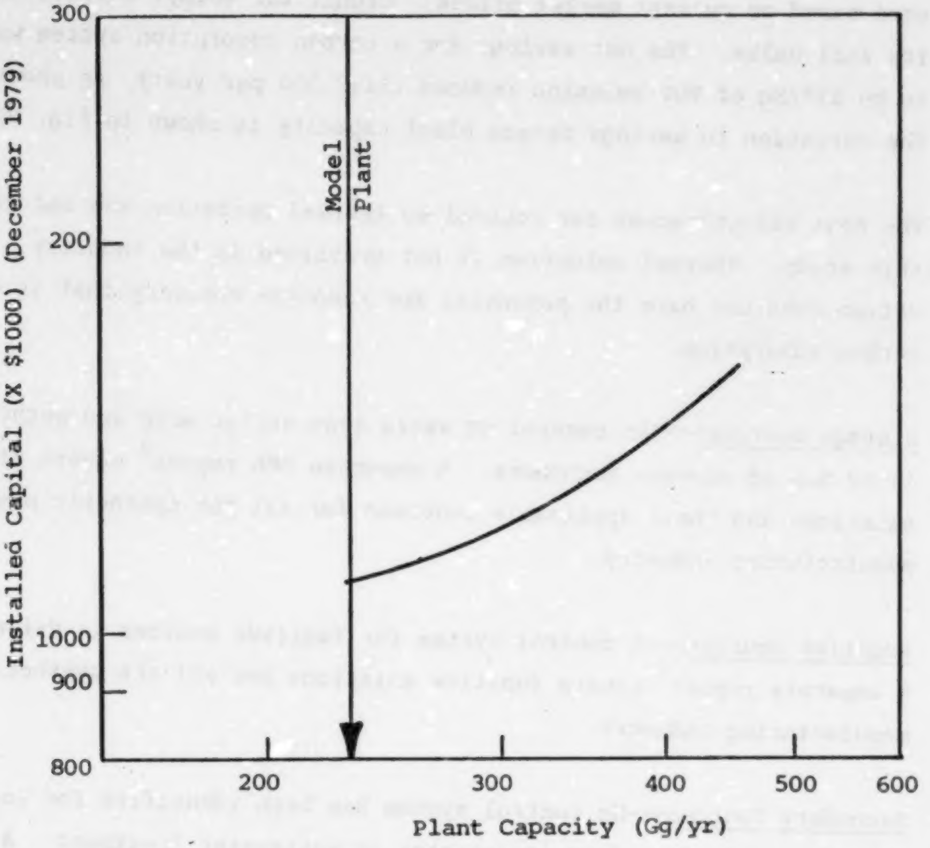

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control by Carbon Adsorption

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To determine the cost effectiveness of a carbon adsorption system, estimates were made of the direct operating cost, of those related to miscellaneous capital, and of capital recovery cost. The recovery credits for acetic acid and p-xylene were based on current market prices;[3] credit for methyl acetate was based on its fuel value. The net savings for a carbon adsorption system was calculated to be $27/Mg of VOC emission reduced ($117,300 per year), as shown by Table VI-4. The variation in savings versus plant capacity is shown in Fig. VI-2.

The cost effectiveness for control by thermal oxidation was not completed for this study. Thermal oxidation is not practiced in the industry. Thermal oxidation does not have the potential for resource recovery that is displayed by carbon adsorption.

b. Storage Sources——The control of vents from acetic acid and methyl acetate storage is by use of aqueous absorbers. A separate EPA report[4] covers storage and handling emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

c. Fugitive Sources——A control system for fugitive sources is defined in Appendix C. A separate report[5] covers fugitive emissions for all the synthetic organic chemicals manufacturing industry.

d. Secondary Sources——No control system has been identified for controlling the secondary emissions from incinerator or wastewater treatment. A separate EPA report[6] covers secondary emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

2. Dimethyl Terephthalate Process

The DMT process emissions are relatively minor and are controlled primarily by xylene absorbers. The cost and cost effectiveness of these absorbers have not been developed for this report.

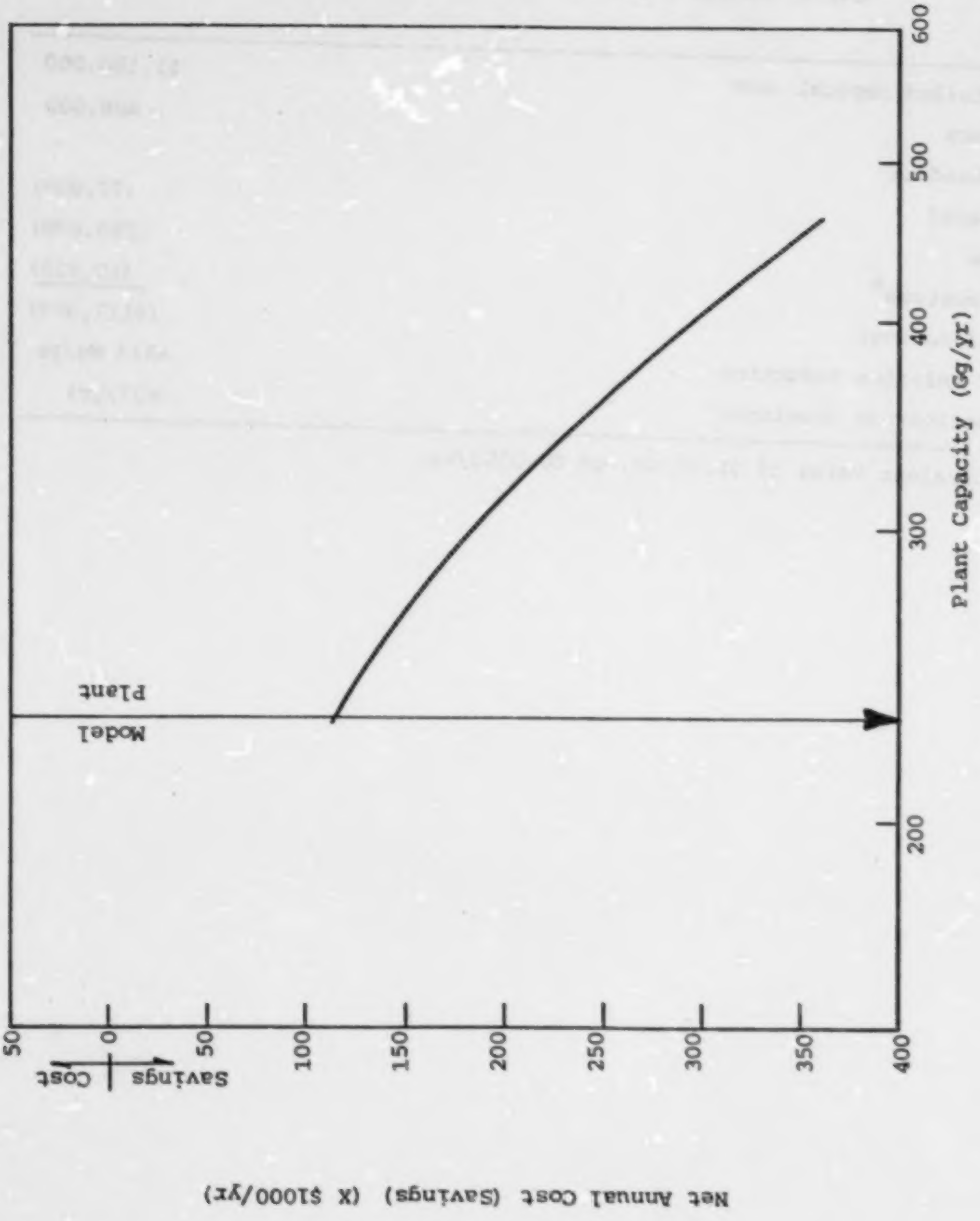

Fig. VI-2. Net Annual Cost (Savings) vs Plant Capacity for Emission Control by Carbon Adsorption

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Table VI-4. Cost-Effectiveness Estimate for Control of Model-Plant C-TPA Process Emissions by Carbon Adsorption

Total installed capital cost	$1,100,000
Annual costs	408,000
Recovery credits	
Acetic acid	(77,800)
p-Xylene	(789,630)
Methyl acetate[a]	(19,520)
Net annual savings	($117,300)
Total VOC emission reduction	4333 Mg/yr
Cost effectiveness (savings)	($27/yr)

[a] Fuel equivalent value of $1.90/GJ, or $0.0083/kg.

C. REFERENCES*

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VII. SUMMARY

Dimethyl terephthalate (DMT) is produced by the esterification purification of crude terephthalic acid (C-TPA).[1] Purified terephthalic acid (P-TPA) is produced by the hydrogenation purification of C-TPA.[2] C-TPA, in turn, is produced by the air oxidation of p-xylene in the presence of acetic acid.[3] DMT is also produced by the air oxidation of a mixture of p-xylene and methyl p-toluate followed by esterification.

The annual growth rate of DMT and P-TPA is estimated to be 6.5 to 9.0%, and production is expected to reach an average of 78 to 86% of capacity for both products by 1982.[3]

Emission sources and uncontrolled and controlled VOC emission rates for the DMT process are given in Table VII-1; there are no VOC emissions from the P-TPA process; the VOC emission sources and rates for C-TPA, the intermediate product, are given in Table VII-2. The current emissions projected for the domestic DMT/P-TPA industry based on the estimated degree of control existing in 1979 are 1.26 Gg of VOC from DMT via C-TPA, no VOC emissions from P-TPA via C-TPA, 28.6 Gg of VOC from C-TPA, and 6.0 Gg of VOC from DMT via the Herofina process.

Control devices for process vents on operating plants include a carbon adsorber in C-TPA production and an o-xylene absorber and refrigerated condenser in DMT production. An emission reduction of 97% or greater may be realized in a carbon adsorber. The installed capital cost of a carbon adsorption system is $1,100,000. The energy requirement for regeneration of the carbon bed and for recovery of the VOC is 16 GJ/hr.

For the carbon adsorption system the cost effectiveness is a net savings of $27/Mg of VOC reduction.

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[1] B. V. Vora et al., "The Technology and Economics of Polyester Intermediates," Chemical Engineering Progress 73(8), 74—80 (August 1977).

[2] AMOCO, Standard Oil Co. (Indiana), Terephthalic Acid and Purified Terephthalic Acid Processes [16-105-P(1-75)] (unpublished report).

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Table VII-1. Emission Summary for Typical Plant Producing Dimethyl Terephthalate via C-TPA (Capacity: 269 Gg/yr)

Emission	Vent Designation (Fig. III-1)	VOC Emission Rate (kg/hr)[a] Uncontrolled	Controlled
Slurry mix tank vents	A	30.72	1.23
Reactor sludge transfer vents	B	b	0.34[c]
Vacuum-jet condenser vent	D	10.44	1.98
Methanol flash still vent	F	0.61	0.61
Storage vents			
Crude DMT	C	2.80	0.028
Methanol	G,H	3.99	0.40
DMT	L	d	5.84[e]
Other storage	I-K	0.92	0.92
Fugitive	M	20.43	5.45
Secondary			
Process boiler	E	0.06	0.06
Incinerator	N-P	NS[f]	NS
Wastewater treatment	Q,R	NS	NS
		69.9	16.8

[a] Based on 8760-hr/yr operation.

[b] Particulate emission of 1.17 kg/hr.

[c] Emission resulting from vaporization of o-xylene scrubbing liquid.

[d] Particulate emission of 5.53 kg/hr.

[e] Emission resulting from vaporization of methanol scrubbing liquid.

[f] Not significant.

Table VII-2. Emission Summary for Model Plant Producing Crude Terephthalic Acid (Capacity: 230 Gg/yr)

Emission	Vent Designation (Fig. III-1)	VOC Emission Rate (kg/hr)* Uncontrolled	VOC Emission Rate (kg/hr)* Controlled
Reactor vent	A	383.3	11.5
Crystallization, separation, and drying vent	B	49.9	1.5
Distillation and recovery vent	C	29.9	0.89
Product transfer vent	D	46.7	1.41
Storage vents			
p-Xylene	F	2.81	2.81
Acetic acid and methyl acetate	G,H,J	0.17	0.003
Propyl acetate	I	0.13	0.036
Fugitive		15.26	4.42
Secondary			
Incinerator	L	0.126	0.126
	M	0.0323	0.0323
Wastewater treatment	N	<0.1	<0.1
		528.4	22.8

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[*] Based on 8760-hr/yr operation.

The emission reduction for the o-xylene absorber on process emissions is 96% and for the refrigerated condenser is 81%. The DMT process emissions are small, and therefore cost and cost effectiveness of these controls have not been developed for this report.

APPENDIX A

Table A-1. Physical Properties of Acetaldehyde*

Synonyms	Acetic aldehyde, ethyl aldehyde
Molecular formula	C_2H_4O
Molecular weight	44.05
Physical state	Liquid
Vapor pressure	123,060 Pa at 25°C
Vapor specific gravity	1.52
Boiling point	20.8°C
Melting point	-121°C
Density	0.7834 at 18°C/4°C
Water solubility	Infinite (hot H_2O)

*From: J. Dorigan *et al*., "Acetaldehyde," p. AI-6 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C)*, MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of Acetic Acid*

Synonyms	Methyl carboxylic acid, ethylic acid, glacial acetic acid, ethanoic acid, vinegar acid
Molecular formula	$C_2H_4O_2$
Molecular weight	60.05
Physical state	Liquid
Vapor pressure	1520 Pa to 20°C
Vapor specific gravity	2.07
Boiling point	117.9°C
Melting point	16.6°C
Density	1.0492 at 20°C/4°C
Water solubility	Infinite

*From: J. Dorigan *et al.*, "Acetic Acid," p. AI-16 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C)*, MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Methanol*

Synonyms	Methyl alcohol, carbinol, methyl hydroxide
Molecular formula	CH_4O
Molecular weight	32.04
Physical state	Liquid
Vapor pressure	17,050 Pa at 25°C
Vapor specific gravity	1.10
Boiling point	64.8°C
Melting point	-93.9°C
Density	0.7913 at 20°C/4°C
Water solubility	Infinite

*From: J. Dorigan *et al*., "Methanol," p. AIII-154 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)*, MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

Table A-4. Physical Properties of Methyl Acetate*

Synonyms	Acetic acid, methyl ester
Molecular formula	$C_3H_6O_2$
Molecular weight	74.08
Physical state	Liquid
Vapor pressure	28,330 Pa at 25°C
Vapor specific gravity	2.55
Boiling point	57.8°C
Melting point	-98.1°C
Density	0.9330 at 20°C/4°C
Water solubility	Very soluble

*From: J. Dorigan _et al_., "Methyl Acetate," p. AIII-148 in _Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)_, MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

Table A-5. Physical Properties of Terephthalic Acid*

Synonyms	p-Phthalic acid, TPA, benzene-p-dicarboxylic acid
Molecular formula	$C_8H_6O_4$
Molecular weight	166.14
Physical state	Solid
Vapor pressure	Negligible
Vapor specific gravity	
Boiling point	Sublimes
Melting point	>300°C sublimes without melting
Density	1.51
Water solubility	Insoluble

*From: J. Dorigan *et al.*, "Terephthalic Acid," p. AIV-174 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals O-Z), MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (Spetember 1976).

Table A-6. Physical Properties of Terephthalic Acid, Dimethyl Ester*

Synonyms	Dimethylterephthalate, DMT, 1,4-benzene dicarboxylic acid, dimethyl ester, dimethyl 1,4-benzene carboxylate dimethyl ester
Molecular formula	$C_{10}H_{10}O_4$
Molecular weight	194.19
Physical state	Solid
Vapor pressure	133.3 Pa at 100°C
Vapor specific gravity	6.70
Boiling point	Sublimes
Melting point	141.0 to 141.8°C
Density	1.194 at 20°C/4°C
Water solubility	Slightly (hot)

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*From: J. Dorigan *et al.*, "Dimethyl Terephthalates," p. AII-162 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals D-E), MTR-7248, Appendix II, Rev. 1, MITRE Corp., Mclean, VA (September 1976).

Table A-7. Physical Properties of o-Xylene*

Synonym	o-Xylol
Molecular formula	C_8H_{10}
Molecular weight	106.2
Physical state	Liquid
Vapor pressure	1,333 Pa at 32.1°C
Vapor specific gravity	3.66
Boiling point	144.4°C
Melting point	-25°C
Density	0.880 at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan *et al.*, "o-Xylene," p. AIV-298 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals O-Z)*, MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

Table A-8. Physical Properties of *p*-Xylene*

Synonym	*p*-Xylol
Molecular formula	C_8H_{10}
Molecular weight	106.2
Physical state	Liquid
Vapor pressure	1,333 Pa at 27.3°C
Vapor specific gravity	3.66
Boiling point	138.5°C
Melting point	13.2°C
Density	0.8611 at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan *et al.*, "*p*-Xylene", p. AIV-300 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals O-Z)*, MTR-7248, Appendix II, Rev. 1, MITRE Corp., Mclean, VA (September 1976).

APPENDIX B

Table B-1. Air-Dispersion Parameters for Crude Terephthalic Acid Model Plant with a Capacity of 230 Gg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
Reactor vent	106.5	20	0.76	311	14.4	31.7
Crystallization, separation, and drying vent	13.9	20	0.1	311	0.045	5.7
Distillation and recovery vent	8.3	20	0.05	311	0.0014	0.71
Product transfer vent	13.0	30	0.46	311	1.76	10.6
Storage vents						
p-Xylene	0.75	12.2				
Acetic acid	0.060	9.8				
Methyl acetate	0.029	7.3				
Propyl acetate	0.012	7.3				
Fugitive*	4.24					
Secondary						
Incinerator	0.044	30	1.58	1250	27.9	14.2
Wastewater	0.028					
			Controlled Emissions			
Carbon adsorber vent	4.25	30	1.22	316	14.4	12.3
Storage vents						
p-Xylene	0.78	12.2				
Acetic acid	0.0002	20				
Methyl acetate	0.001	20				
Propyl acetate	0.008	7.3				
Fugitive*	1.25					
Secondary						
Incinerator	0.044	30	1.58	1250	27.9	14.2
Wastewater	0.028					

*Fugitive emissions are distributed over an area of 100 m X 200 m.

Table B-2. Air-Dispersion Parameters for Typical Plant for Dimethyl Terephthalate with a Capacity of 269 Gg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
Slurry mix tank vent	8.53	20	0.05	311	0.006	3.0
Reactor sludge transfer vent	a					
Vacuum-jet condenser vent	2.90	20	0.10	311	0.035	1.5
Methanol flash still vent	0.17	20	0.05	311	0.0002	0.1
Storage vents						
Crude DMT	0.78	20				
Methanol	1.11	9.8				
DMT						
Other storage	0.26	7.3				
Fugitive [b]	5.71					
Secondary						
Process boiler	0.017					
Incinerator	Nil					
Wastewater	Nil					
			Controlled Emissions			
Slurry mix tank vent	0.34	20	0.05	311	0.006	3.0
Reactor sludge transfer vent	0.094	20	0.05	311	0.0002	0.1
Vacuum-jet condenser vent	0.54	20	0.10	293	0.035	1.5
Methanol flash still vent	0.17	20	0.05	311	0.0002	0.1
Storage vents						
Crude DMT	0.0078					
Methanol	0.11					
DMT	1.62					
Other storage	0.26					
Fugitive [b]	1.5					
Secondary						
Process boiler	0.017					
Incinerator	Nil					
Wastewater	Nil					

[a] Particulate emissions only.

[b] Fugitive emissions are distributed over an area of 150 m X 200 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATING PROCEDURES

A. CRUDE TEREPHTHALIC ACID PROCESS——CARBON ADSORPTION (CA) SYSTEM COST ESTIMATE

As shown by Table IV-1 the total VOC flow from vents A, B, C, and D equals 509.8 kg/hr. The total gas flow from these vents is estimated to be 72,900 kg/hr, which equals 34,000 scfm. The average VOC molecular weight is approximately 84, the estimated VOC concentration is 2360 ppm_v, and the estimated loading capacity is 15 lb of VOC/100 lb of carbon. From Fig. II-1 of the control device evaluation report for carbon adsorption,[1] 3.7 lb of carbon are required/1000 scf of waste gas. The total carbon requirement is therefore

$$\frac{3.7\ \text{lb C}}{1000\ \text{scf}}\ \frac{34{,}000\ (60)\ \text{scf}}{\text{hr}}\ \frac{3\ \text{hr}}{\text{cycle}} = \frac{22{,}500\ \text{lb of C}}{\text{cycle}}\ .$$

From Fig. IV-1 of the carbon adsorption report the December 1979 installed capital for a 34,000-scfm CA system is $750,000. To adjust the cost for stainless steel requirements a 1.5 adjustment was applied to the installed cost except for the initial carbon. The total installed cost preliminary estimate is $1,100,000, including the carbon cost for three beds. Figure IV-3 in the carbon adsorption report indicates the annual cost to be $12/scfm, or $408,000.

The annual cost adjustments for fixed costs associated with the added capital for stainless steel construction, the added utilities for product recovery separation, and the equivalent raw-material recovery credits are included in Table D-1.

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[1] H. S. Basdekis and C. S. Parmele, IT Enviroscience, Inc., Control Device Evaluation. Carbon Adsorption (January 1981) (EPA/ESED report, Research Triangle Park, NC).

Table D-1. Carbon Adsorption Control Cost Summary

	Capacity		
	Model Plant 230 Gg/yr (34,000 scfm)	Model Plant 350 Gg/yr (51,740 scfm)	Model Plant 450 Gg/yr (66,520 scfm)
Total installed capital	$1,100,000	$1,300,000	$1,600,000
Annual cost[a]	$408,000	$595,000	$732,000
Fixed cost for extra capital	101,500	119,000	145,000
Utilities for recovery distillation	260,150[b]	395,900	509,000
Recovery credits			
Acetic acid	(77,800)	(118,390)	(152,220)
p-Xylene	(789,630)	(1,201,610)	(1,544,930)
Methyl acetate	(19,520)	(29,700)	(38,190)
Net annual cost	($117,300)	($239,800)	($349,340)
VOC emission reduction	4333 Mg/yr	6593 Mg/yr	8478 Mg/yr
Cost effectiveness (savings) per Mg of VOC reduced)	($27.07)	($36.37)	$41.21)

[a] From Fig. IV-3 of the carbon adsorption report.

[b] Azeotropic distillation: steam $232,140; cooling water $28,010.

APPENDIX E

EXISTING PLANT CONSIDERATIONS

Tables E-1 and E-2[1—5] list process control devices reported to be in use by industry. To gather information for the preparation of this report three site visits were made to manufacturers of terephthalic acid and dimethyl terephthalate. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Research Triangle Park, NC.[1,3,4] Some of the pertinent information concerning process emissions from these existing terephthalic acid and dimethyl terephthalate plants is presented in this appendix.

A. PROCESS EMISSIONS FROM EXISTING PLANTS

1. Hercofina Hanover Plant, Wilmington, NC[4]

Hercofina manufactures dimethyl terephthalate by the Hercules-Imhausen-Witten process. In this process p-xylene and recycled methyl toluate are oxidized with air to form toluric acid, monomethyl terephthalate, and terephthalic acid. This mixture is esterified to produce dimethyl terephthalate. p-Xylene and pure methanol are received by barge. Reclaimed methanol is received by tank car and tank truck.

The main emission from the process, oxidizer off-gas, is due to the large amount of nitrogen present as a result of air oxidation. The emission is controlled by a carbon adsorption system (see Table E-3). Several processing steps involve the use of methanol. The emissions from the processing steps are collected by the methanol recovery header and fed to the methanol recovery absorber for emission control before being released to the atmosphere (see Table E-3). A portion of the DMT produced is converted to a solid form by being passed through a flaker. Emissions from the flaker are discharged to the atmosphere (see Table E-3).

Water is a by-product of the oxidation of p-xylene and the esterification of toluic and terephthalic acids. After appropriate decantation and stripping, the wastewater (containing soluble, nonstrippable organics) is sent to the thermal oxidizer for disposal (see Table E-4). Residues formed throughout the process resulting from oxidation and distillation are discharged and disposed of by incineration at the site (see Table E-4).

Table E-1. Emission Control Devices Currently Used by Terephthalic Acid Producers

Source	Control Devices in Use				
	By Amoco[a]	By Du Pont, Cape Fear[b]	By Du Pont, Hickory[b]	By Eastman, Carolina[c]	By Hercofina[d]
Reactor vent	None[e]	None[e]	None[e]	None[e,f]	Carbon adsorber
Crystallization, separation, drying vent	Aqueous absorber	Aqueous absorber	Aqueous absorber	Aqueous absorber	NA[g]
Distillation and recovery vent	None	Aqueous absorber	Aqueous absorber	Aqueous absorber	NA
Product transfer vent	Bag filter	Bag filter	Bag filter	Bag filter	NA
Storage vents					
p-Xylene	Conservation vent	Conservation vent	Double-seal floating roof	Conservation vent	Conservation vent
Acetic acid	Aqueous absorber	Aqueous absorber	Aqueous absorber	NA	NA

[a] See ref 1.

[b] See ref 2.

[c] See ref 3.

[d] See ref 4.

[e] High-pressure absorber is considered to be a part of basic process.

[f] A small side stream is passed through a carbon adsorber for organic removal.

[g] Not applicable.

Table E-2. Emission Control Devices Currently Used by Dimethyl Terephthalate Producers

Source	Control Devices in Use				
	By Eastman, Carolina[a]	By Eastman, Tennessee[b]	By Du Pont, Cape Fear[c]	By Du Pont, Hickory[c]	By Hercofina[d]
Slurry mix tank vent	None	Conservation vent	Hydrocarbon scrubber and vent condenser	Hydrocarbon scrubber and vent condenser	NA[e]
Reactor sludge transfer vent	Water scrubber	Water scrubber	Hydrocarbon scrubber	Hydrocarbon scrubber	NA
Crude DMT tank vent	Xylene absorber	Conservation vent	Hydrocarbon scrubber	Hydrocarbon scrubber	NA
Methanol recovery still, low-boiler still vents	Burned as fuel	Burned as fuel	Burned as fuel	Burned as fuel	Carbon adsorber
Methanol flash still	None	Conservation vent	Conservation vent	Conservation vent	Water absorber
Storage					
Methanol	Conservation vent	Conservation vent	Water absorber	Double seal floating-roof, conservation vent	Floating roof
o-Xylene	Conservation vent	Conservation vent	Conservation vent	Conservation vent	NA
MPTB, MFB	Conservation vent	Conservation vent	ND[f]	Bag filter	NA
DMT	Methanol absorber	Methanol absorber	Hydrocarbon vortex scrubber	Hydrocarbon scrubber	Methanol scrubber
MFB, MPTB waste	Incinerator	Incinerator	ND	ND	NA
Sludge waste	Incinerator	Incinerator	Boiler	Incinerator	ND
Wastewaters	Wastewater treatment	Wastewater treatment	Wastewater treatment	Wastewater treatment	Incinerator

[a] See ref 3.
[b] See ref 5.
[c] See ref 2.
[d] See ref 4.
[e] Not applicable.
[f] No data.

Table E-3. Direct Emissions (Hercofina Hanover Plant)

Emission Source	Vent to:	Pollutant	Pollutant Flow (lb/1000 lb of Product) Before ECD[a]	Pollutant Flow (lb/1000 lb of Product) After ECD[a]
Emergency reactor pressure relief	Atmosphere	p-xylene/oxidate	None	None
Oxidizer off-gas	Carbon adsorption column	p-xylene	28	0.93
		Light VOC	60	12.06
Xylene-water decanter and storage	Condenser	p-xylene	No data	No data
Process tank vents	Xylene vent scrubber	Aromatic methyl esters and xylene	36	
Emergency relief	Atmosphere	Methanol or wastewater	None	None
Methanol recovery header	Methanol recovery absorber	Methanol	68	1
Vacuum jet barometric tank	Atmosphere	VOC	No data	No data
Emergency relief	Atmosphere	Aromatic methyl esters	None	None
DMT crystallization melt tank, emergency	Atmosphere	Methanol	None	None
DMT flaker	Atmosphere	Light ends	0.2	0.2
DMT dust vent	DMT dust collector	DMT dust	5.02	0.03

[a] Emissions control device.

Table E-4. Secondary Emissions (Hercofina Hanover Plant)

			Pollutant Flow (lb/1000 lb of Product)	
Potential Emission Source	Discharged to	Pollutant	Pollutant Rate	Stream Rate
Wastewater	Incinerator	HOAC	12	281
		Formic acid	4	
		Formaldehyde	4	
		Methanol	1	
DMT finishing still residue	Disposal	No data	No data	No data

Table E-5 lists the information received on emission control devices.

2. Carolina Eastman Company, Columbia, SC[3]

Carolina Eastman Company at Columbia, SC, manufactures terephthalic acid (TPA) and uses it as a raw material in the manufacture of dimethyl terephthalate (DMT). The facilities at this site also include processes for converting DMT to polyester products. The TPA processing steps are conducted in multiple units, including six oxidizers, that are operated interchangeably depending on product demand and maintenance needs. The DMT process is a single-train design. These facilities were put into operation starting in Novermber 1976.

p-Xylene, acetaldehyde, and fresh methanol are received by tank car. Recycle methanol is transferred by pipeline from the polymer plant, where it is released from DMT by transesterification with a glycol. TPA is conveyed by low-oxygen gas from the TPA plant to the DMT plant. DMT is transferred by pipeline to the polymer plant.

The TPA process used at the Columbia plant is the cobalt bromide—catalyzed air oxidation of p-xylene in the presence of acetic acid. The main discharge from the process is the result of using air for oxidation. The reactor off-gas is passed through a water absorber for recovery and control of emissions. A small amount of low-oxygen gas is produced by passing the scrubbed gas through a carbon adsorption bed. Some of the scrubbed gas is used to convey the product to storage and is discharged to the atmosphere after it is passed through a bag filter. The remainder is discharged directly to the atmosphere (see Table E-6).

The emission from the distillation and recovery of low boilers is sent to an absorber for emission control before being discharged to the atmosphere (see Table E-6). Small amounts of VOC emission are released during water-removal distillation and during filtration and drying.

Emissions can result from the handling and disposal of wastewater from the diltillation system. This stream may contain small amounts of methyl acetate, n-propyl acetate, and acetic acid.

Table E-5. Emission Control Devices (Hercofina Hanover Plant)

Emission Control Device	Pollutant	Control Efficiency (%)	Control Agent	Size	Cost ($/M lb of Product) Capital	Cost ($/M lb of Product) Annual Operating
Carbon adsorber	*p*-xylene, light VOC	97, 80	Active carbon	Two 9.5-ft diam, X 22 ft long	1.05/M lb[a]	0.55[b]
Solvent scrubber	*p*-xylene, other VOC	97	Xylene	1750-gal tank 750-ft^2 condenser	0.21[a]	0.11[b]
Thermal oxidizer w/heat recovery	Acetic acid Formic acid Formaldehyde Methanol	~100	Fire	140 MM Btu/hr	3.97[c]	0.88[d]
Chilled solvent scrubber	Methanol	99	Chilled	6000-ft^2 condenser	0.61[a]	0.32[b]
	Light ends		Solvent	483-ft^2 cooler		
Dust collector	DMT dust	99	Bag filter	8000 cfm	0.47[c]	0.16[e]

[a] 1972 basis.

[b] 1977 basis.

[c] 1973 basis.

[d] 1975 basis.

[e] Year not known.

Table E-6. Direct Emissions from TPA Manufacture (Carolina Eastman)

Emission Source	Emission Control Device	Pollutant	Pollutant Flow (lb/1000 lb of Product) Before ECD[a]	After ECD[a]
Reactor off-gas	Solvent absorber	MeOAc, p-xylene, MeBr, acetalydehyde, methanol	ND[b]	4.26
		CO	ND[b]	11.2
Low-boiler distillation	Solvent absorber	MeOAc	ND[b]	0.035
Decanter vent	Atmosphere	Propylacetate	0.0038	0.0038
Solids transport vent	Dust collector	TPA particulate	ND[b]	b
		VOC	ND[b]	0.38[c]
		CO	ND[b]	1.72[c]
Filter vent	Solvent absorber	Acetic acid	ND[b]	0.0017

[a] Emission control device.

[b] No data.

The process for the manufacture of DMT at the Carolina Eastman Columbia plant is the direct esterification of crude terephthalic acid with methanol. Emissions from the slurry mix tank vents are caused by filling losses from batch preparation. The discharges from the slurry feed tank vents are also caused by filling losses from batch feed preparation. The discharge from the jet seal pot is caused by air in-leakage during vacuum distillation. The discharges from the sludge hoods are caused by evaporation losses during transfer of reactor sludge from the stripper into containers used for transferring material to sales or to landfill (see Table E-7).

The esterification process results in the formation of low-boiling materials such as dimethyl ether and methyl acetate, which are handled by pipeline and are disposed of in a fired boiler. It is estimated that the destruction is essentially 100%. The by-products MPTB and MFB are also disposed of by burning.

Wastewater containing unknown amounts of VOC is discharged to the wastewater system, and emissions can result from the handling and disposal of these materials. The sources of this water are water formed in esterification, steam from jets, and water from the scrubber on the sludge discharge hood.

3. Amoco Chemicals Corp., Decatur, AL[1]

The process used at Decatur for the manufacture of terephthalic acid is the continuous air oxidation of p-xylene in acetic acid solution. The first TA plant at Decatur was built in 1966, and the last unit was completed ten years later. p-Xylene is received by barge, and makeup acetic acid is received by tank car. The PTA product is a solid and is shipped by rail car.

The main discharge from the process is due to the large amount of nitrogen present as the result of air oxidation. The emission is passed through a high-pressure water absorber before being released to the atmosphere (see Table E-8).

VOC discharges result from the venting of dissolved inert gases present in the liquid leaving the reactor under reactor pressure (see Table E-8). A minor discharge results from miscellaneous process vents controlled by a low-pressure absorber (see Table E-8).

Table E-7. Direct Emissions from Dimethyl Terephthalate Process (Carolina Eastman)

Emission Source	Emission Control Device	Pollutant	Pollutant Flow (lb/1000 lb of Product) Before ECD	After ECD
TA slurry mix tanks, vents	Atmosphere	MeOH, o-xylene	0.0090	0.0090
TA slurry feed tanks, vents	Atmosphere	MeOH, o-xylene	0.0186	0.0186
Vent from sludge recovery	Contact condenser	o-Xylene, others	0.0913	0.0084
Decanter	Atmosphere	o-Xylene	7×15^{-6}	$7\text{X}\ 10^{-6}$
Jet seal pot vent	Atmosphere	o-Xylene	$3\ \text{X}\ 10^{-7}$	$3\ \text{X}\ 10^{-7}$
Product transfer	Solvent absorber	DMT	0.171	
		MeOH	0.0113	0.146
Sludge hood vent	Scrubber	Particulate	12 g/m^3	2.97 mg/m^3
Sludge hood vent	Scrubber	Particulate	15 g/m^3	1.25 mg/m^3

Table E-8. Direct Emissions TPA (Amoco, Decatur, AL)

Emission Source	Emission Control Device	Pollutant	Pollutant Flow (lb/1000 lb of Product)	
			Before ECD	After ECD
Emergency vent	Atmosphere[a]	Acetic acid	0.04	0.04
		p-xylene		
Nitrogen vent	High pressure absorber	Acetic acid		0.72
		Methyl acetate	N.D.[b]	9.0
		p-xylene		2.95
Crystallizer	Atmosphere[a]	Acetic acid	2.1	2.1
Process vent	Low pressure absorber	Acetic acid	0.23	0.01
		Methyl acetate	N.D.	Trace
Dehydration tower	Atmosphere[a]	Acetic acid	Trace	Trace
		Methyl acetate	4.1	4.1
		p-xylene	Trace	Trace

[a] No emission control device.

[b] No data.

The inorganic portions of the catalyst, the by-products and residues formed in the reaction and distillation sections, and the unrecoverable portions of the product are carried through the process in the liquid phase and are ultimately discharged as the residue from the residue still. This stream contains some acetic acid, which is disposed of in a rotary kiln incinerator.

4. Du Pont and Co., Cape Fear, NC, and Old Hickory, TN[2]

The emission factor data presented here represent annual averages for the combined TPA and DMT processes at each location.

	TPA (lb of VOC/CWT)	DMT (lb of VOC/cwt)
High-pressure absorber vents	2.03	
Atmospheric absorbers	0.027	
Silo bag filters	0.21	
TPA process incinerators	Neg.	
Methanol column vents		0.037
Vacuum-jet condenser vents		0.035

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

C. REFERENCES*

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2. D. W. Smith, E. I. du Pont de Nemours and Co., letter dated Oct. 20, 1978, in response to EPA's request for information on emissions from TPA/DMT production facilities.

3. S. W. Dylewski, IT Enviroscience, Inc., Trip Report for Visit to Carolina Eastman Co., Columbia, SC, Dec. 6, 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. S. W. Dylewski, IT Enviroscience, Inc., Trip Report for Visit to Hercofina Co., Wilmington, NC, Nov. 17, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. J. C. Edwards, Tennessee Eastman Co., letter dated Aug. 31, 1978, in response to EPAs request for information on TPA/DMT production facilities.

6. L. M. Elkin, Terephthalic Acid and Dimethyl Terephthalate, pp 49—55 in Report No. 9, A private report by the Process Economics Program, Stanford, Research Institute, Menlo Park, CA (February 1966).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 6

PHENOL/ACETONE

C. W. Stuewe
F. D. Hobbs

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Production of acetone and phenol was selected for study because their manufacture results in significant emissions of volatile organic compounds (VOC). A major portion of both acetone and phenol domestic production is based on the cumene peroxidation process. As of 1978, 67% of domestic acetone production was based on this process, with most of the remainder being derived from isopropyl alcohol.[1] A small amount of listed capacity is derived as by-product of other products, including 2-naphthol, hydroquinone, and propylene oxide.[2] As of 1978, 94% of the listed domestic synthetic phenol capacity was based on the cumene peroxidation process, with the remaining synthetic phenol capacity being based on the benzene sulfonation process and the toluene oxidation process.[3] A small amount (less than 2% of the total domestic production in 1974) of phenol, called natural phenol, is recovered from coal tar and petroleum streams.[3]

VOC emissions from the cumene peroxidation process include acetone, cumene, phenol, acetaldehyde, and α-methylstyrene. VOC emissions from the isopropyl alcohol process include acetone and isopropyl alcohol. Acetone constitutes the major VOC in emissions from both the cumene peroxidation process and the isopropyl alcohol process because of the volatility of that VOC (see Appendix A for pertinent physical properties).

Although the isopropyl alcohol process is included in the above discussion for completeness, the subject of this report is the cumene peroxidation route to phenol and acetone. In the following sections processes other than cumene peroxidation are described only briefly, and discussions of emissions, emission controls, and control impacts are exclusively devoted to the cumene peroxidation process.

B. ACETONE USAGE AND GROWTH

Table II-1 shows the acetone end products, the percentages of total consumption, and the projected growth rates. The largest single consumption of acetone is in production of methyl methacrylate, which is converted to acrylic sheet. The next largest acetone consumer is methyl isobutyl ketone production, but this use is declining because of environmental legislation restrictions on the use of methyl

Table II-1. Acetone Usage and Growth[a]

End Use	1977 Production (%)	Average Annual Growth (%) 1977-1982
Methyl methacrylate	25	7.0-8.0
Methyl isobutyl ketone	9	(2.5-3.5)
Bisphenol A	6	10.0-11.0
Methacrylic acid and higher methacrylate	5	7.0-8.0
Methyl isobutyl carbinol	2	0.0-2.0
Aldol chemicals	9	2.5-3.5
Solvent uses	22	3.0-3.5
Miscellaneous	22	3.0-3.5

[a] See ref 1.

isobutyl ketone as a solvent. Consumption for production of bisphenol A, which is used for epoxy and polycarbonate resins manufacture, is expected to increase rapidly.[4]

Domestic acetone capacity in 1978 was reported[3] to be about 1326 Gg/yr, with reported[5] 1978 production utilizing about 71% of that capacity. Production would reach 83—86% of current capacity by 1982 based on the projected[4] 4 to 5% annual growth rate.

C. PHENOL USAGE AND GROWTH

Table II-2 shows the phenol end products, the percentages of total consumption, and the projected growth rates.

The largest consumer of phenol is phenolic resins, which are used as adhesives. The second largest use of phenol is an intermediate for bisphenol A, which is used in the manufacture of epoxy resins. Large amounts of phenol are used to manufacture cyclohexanone, which is converted to caprolactam through a series of reactions. Caprolactam is used in the production of nylon fibers.[6]

Domestic phenol capacity in 1978, including natural phenol, was reported[3] to be 1624 Gg/yr, with 1978 production[7] utilizing about 77% of that capacity. Production would reach about 92% of current capacity by 1982 based on the projected[8] 4.5% annual growth rate.

D. DOMESTIC PRODUCERS

As of the end of 1977 there were 15 producers of acetone, as listed in Table II-3, at the plant locations shown in Fig. II-1 and 12 producers of synthetic phenol, listed in Table II-4, at the plant locations shown in Fig. II-2. Six producers separate natural phenol from coal tar and petroleum; they are listed in Table II-4 but are not shown in Fig. II-2. Following are brief descriptions of those companies producing acetone and phenol.

1. Allied

Acetone and phenol are produced by cumene peroxidation. Phenol is used in the production of adipic acid and cyclohexanone for caprolactam. Some phenol is sold.[6]

Table II-2. Phenol Usage and Growth[a]

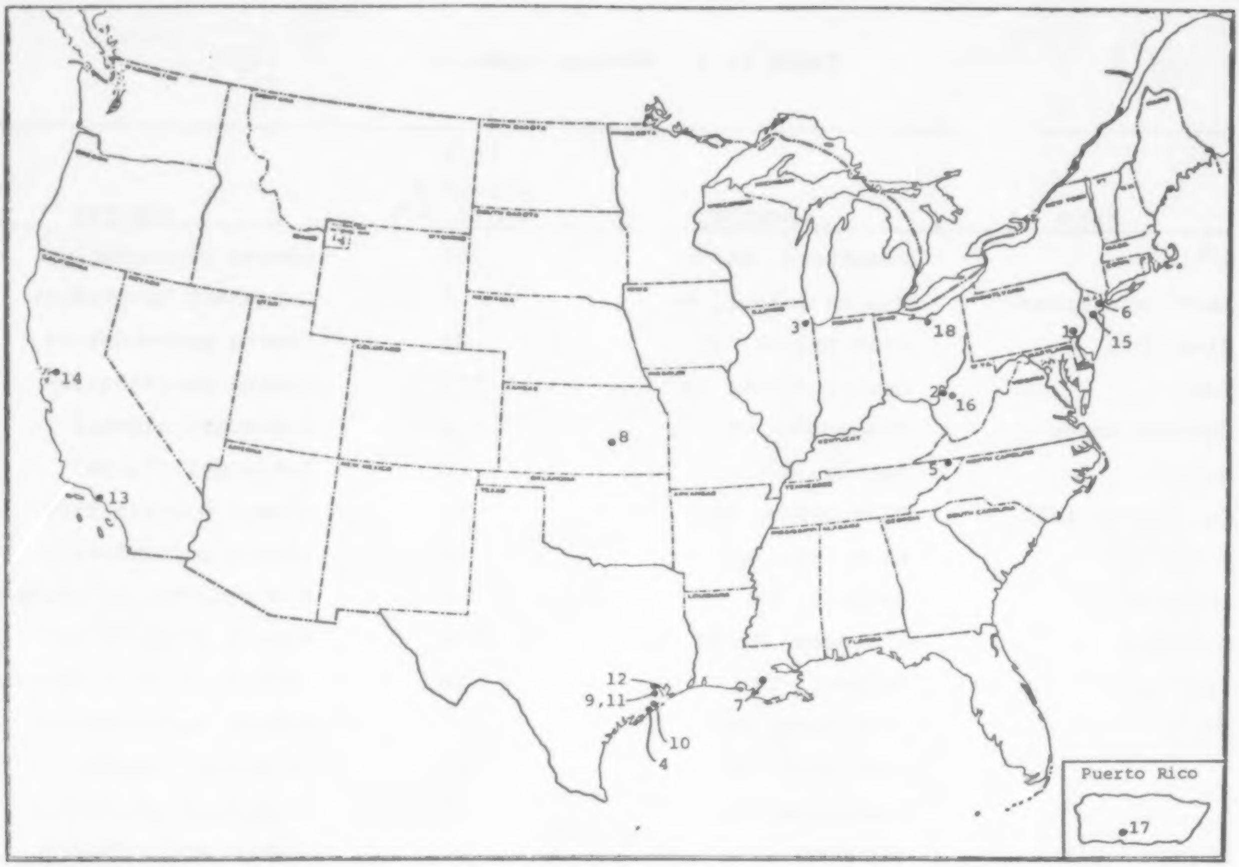
End Use	1977 Production (%)	Average Annual Growth (%) 1977-1982
Phenolic resins	44	3.5-4.5
Bisphenol A	17	10.0-11.0
Caprolactam	15	5.0-5.5
Nonylphenol	2	4.0-5.0
Salicylic acid	1	2.5-4.5
Dodecylphenol	1	1.5-2.5
Adipic acid	1	1.5-2.5
Miscellaneous	19	4.0-5.0

[a] See ref 6.

Table II-3. Acetone Capacity[a]

Plant	Location	1978 Capacity (Mg, X 10^3)	Process
Allied	Frankford, PA	163	Cumene peroxidation
American Cyanamid	Willow Island, WV	5	2-Naphtol by-product
Clark Oil	Blue Island, IL	24	Cumene peroxidation
Dow	Oyster Creek, TX	127	Cumene peroxidation
Eastmen Kodak	Kingsport, TN	36	Isopropyl alcohol
Exxon	Bayway, NJ	63	Isopropyl alcohol
Georgia-Pacific	Plaquemine, LA	71	Cumene peroxidation
Getty Oil	El Dorado, KS	25	Cumene peroxidation
Goodyear	Bayport, TX	5	Hydroquinone by-product
Monsanto	Chocolate Bayou, TX	136	Cumene peroxidation
Oxirane	Bayport, TX	18	Propylene oxide by-product
Shell	Deer Park, TX	136	Cumene perioxidation
	Deer Park, TX	181	Isopropyl alcohol
	Dominquez, CA	45	Isopropyl alcohol
Standard Oil	Richmond, CA	15	Cumene peroxidation
Union Carbide	Bound Brook, NJ	50	Cumene peroxidation
	Institute and South Charleston, WV	77	Isopropyl alcohol
	Penuelas, PR	59	Cumene peroxidation
United States Steel	Haverhill, OH	90	Cumene peroxidation
Total		1326	

[a] See ref 2.



1. Allied Chemical Corp., Frankford, PA
2. American Cyanamid Co., Willow Island, WV
3. Clark Oil & Refining Corp., Blue Island, IL
4. Dow Chemical Co., Oyster Creek, TX
5. Eastman Kodak Co., Kingsport, TN
6. Exxon Corp., Bayway, NJ
7. Georgia-Pacific Corp., Plaquemine, LA
8. Getty Oil Co., El Dorado, KS
9. Goodyear Tire & Rubber Co., Bayport, TX
10. Monsanto Co., Chocolate Bayou, TX
11. Oxirane Corp., Bayport, TX
12. Shell Chemical Co., Deer Park, TX
13. Shell Chemical Co., Dominquez, CA
14. Standard Oil Co. of CA, Richmond, CA
15. Union Carbide Corp., Bound Brook, NJ
16. Union Carbide Corp., Institute and South Charleston, WV
17. Union Carbide Corp., Penuelas, PR
18. United States Steel Corp., Haverhill, OH

Fig. II-1. Locations of Plants Manufacturing Acetone

Table II-4. Phenol Capacity[a]

Plant	Location	1978 Capacity (Mg) (X 10^3)	Process
Allied Chemical	Frankford, PA	272	Cumene peroxidation
Clark	Blue Island, IL	40	Cumene peroxidation
Dow	Oyster Creek, TX	211	Cumene peroxidation
Fallik Chemical	Tuscaloosa, AL	b	Unknown (natural phenol)
Ferro	Santa Fe Springs, CA	c	Coal tar and petroleum
Georgia-Pacific	Plaquemine, LA	118	Cumene peroxidation
Getty Oil	El Dorado, KS	43	Cumene peroxidation
Kalama	Kalama, WA	34	Toluene oxidation
Koppers	Follansbee, WV	b	Coal tar
Merichem	Houston, TX	b	Petroleum
Monsanto	Chocolate Bayou, TX	227	Cumene peroxidation
Reichhold	Tuscaloosa, AL	70[d]	Benzene sulfonation
Shell	Deer Park, TX	227	Cumene peroxidation
Standard Oil	Richmond, CA	25	Cumene peroxidation
Stimson	Anacortes, CA	b	Petroleum
Union Carbide	Bound Brook, NJ	82	Cumene peroxidation
	Penuelas, PR	100	Cumene peroxidation
U.S. Steel Corp.	Clairton, PA	c	Coal tar
	Haverhill, OH	148[e]	Cumene peroxidation
Total		1,624	

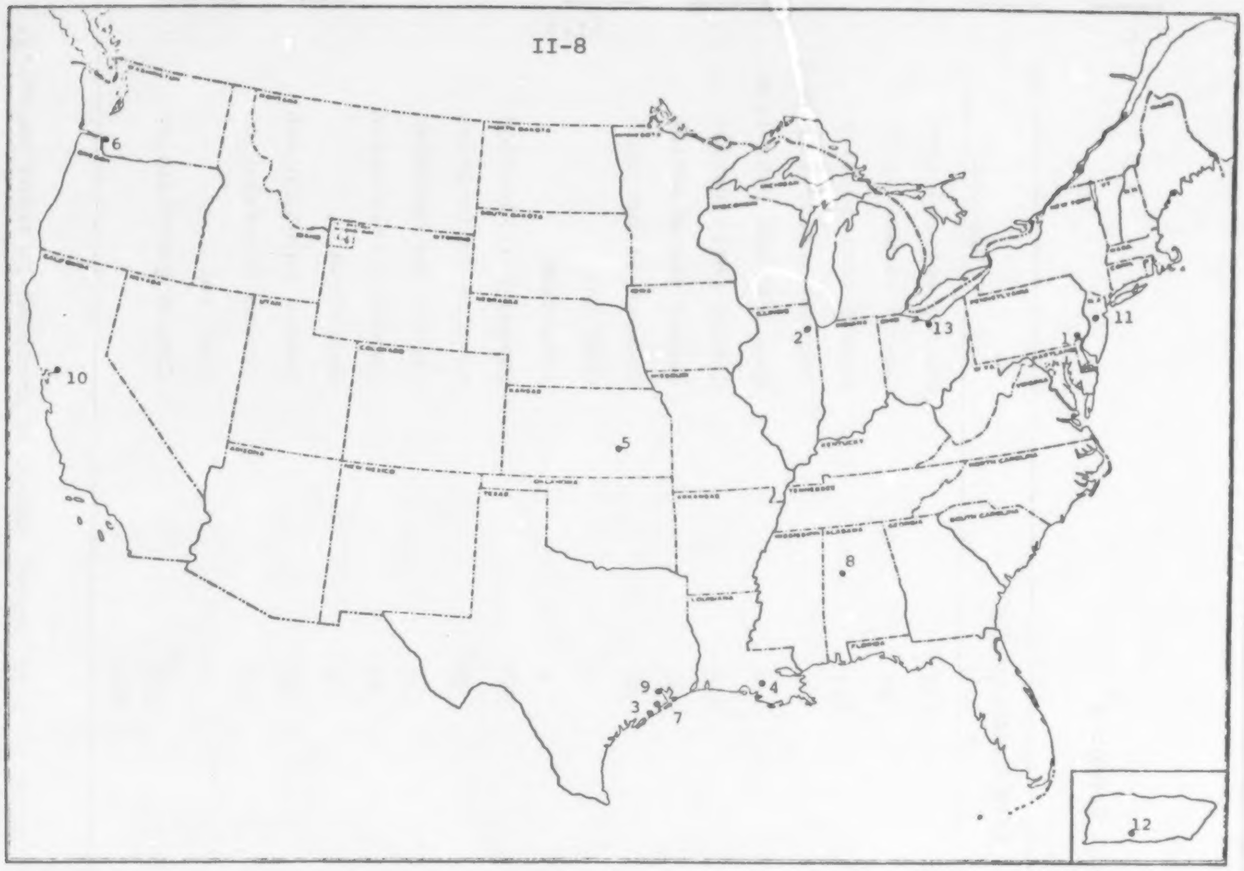
[a] See ref 3.

[b] These four plants combined have a natural-phenol capacity of about 27 X 10^3 Mg/yr, which is included in total capacity.

[c] Not available.

[d] Closed; placed on standby in March 1978.

[e] Capacity recently increased by 195 X 10^3 Mg/yr.



1. Allied Chemical Corp., Frankford, PA
2. Clark Oil & Refining Corp., Blue Island, IL
3. Dow Chemical Co., Oyster Creek, TX
4. Georgia-Pacific Corp., Plaquemine, LA
5. Getty Oil Co., El Dorado, KS
6. Kalama Chemical Co., Kalama, WA
7. Monsanto Co., Chocolate Bayou, TX
8. Reichhold Chemicals, Inc., Tuscaloosa, AL
9. Shell Chemical Co., Deer Park, TX
10. Standard Oil Co. of CA, Richmond, CA
11. Union Carbide Corp., Bound Brook, NJ
12. Union Carbide Corp., Penuelas, PR
13. United States Steel Corp., Haverhill, OH

Fig. II-2. Locations of Plants Manufacturing Phenol

2. American Cyanamid

   Acetone is produced as a by-product of 2-naphthol.[2]

3. Clark Oil

   Acetone and phenol are produced by cumene peroxidation. Phenol is mainly sold, but some is used in production of phenolic resins.[6]

4. Dow

   Acetone and phenol are produced by the cumene peroxidation process.[6]

5. Eastman Kodak

   Acetone is produced from isopropyl alcohol.[2]

6. Exxon

   Acetone is produced from isopropyl alcohol.[2]

7. Fallek

   Natural phenol is recovered from an unreported feed stock.[3]

8. Ferro

   Natural phenol is recovered from coal tar and petroleum streams.[3]

9. General Electric

   General Electric, which is not listed in the tables of producers as a current producer, plans to build a cumene-based phenol/acetone plant with 100-Gg/yr acetone capacity and 181-Gg/yr phenol capacity at Mount Vernon, IN, beginning in 1980.[8–10]

10. Georgia-Pacific

    Acetone and phenol are produced by cumene peroxidation. About 50% of the phenol is sold and the remainder is consumed in the production of phenolic resins.[6]

11. Getty Oil

    Acetone and phenol are produced by cumene peroxidation.[2,3]

12. Goodyear

Acetone is produced as a by-product of hydroquinone.[2]

13. Gulf Oil

Gulf Oil, which is not listed in the tables as a current producer, plans to have a plant completed in 1981[8,9] that will have an acetone capacity of 136 Gg/yr and a phenol capacity of 227 Gg/yr.

14. Kalama

Phenol is produced by toluene oxidation.[3] It was reported[8] that the capacity would be expanded by 9 Gg/yr in 1978.

15. Koppers

Natural phenol is separated from coal tar.[3]

16. Merichem

Natural phenol is separated from petroleum.[3]

17. Monsanto

Acetone and phenol are produced by cumene peroxidation. The phenol is used as an intermediate for manufacture of a number of different chemicals and also is sold.[6]

18. Oxirane

Acetone is produced as a by-product of propylene oxide.[2]

19. Reichold

Phenol was produced by benzene sulfonation to produce phenolic resins, pentachlorophenol, and miscellaneous chemicals, as well as for sale.[6] This capacity was placed on standby in March 1978.

20. Shell

Acetone and phenol are produced by cumene peroxidation at the Deer Park, TX, plant.[3] Acetone is produced from isopropyl alcohol at Deer Park, TX, and Dominguez, CA. A new acetone plant with 136-Gg/yr capacity is due to be completed at Wood River, IL, in 1979.[9] Acetone was produced by oxidation of isopropyl alcohol at the Norco, LA, plant, but that process has been permanently shut down. All acetone produced from isopropyl alcohol by Shell is now produced by the dehydrogenation process.[11]

21. Standard Oil
Acetone and phenol are produced by cumene peroxidation. Phenol is used for the manufacture of alkylphenols. Some of the phenol is sold.[6]

22. Stimson Lumber
Natural phenol is separated from petroleum.[3]

23. Union Carbide
Acetone and phenol are produced by cumene peroxidation at the Bound Brook, NJ, and Penuelas, PR, plants.[3] Acetone also is produced from isopropyl alcohol at Institute and South Charleston, WV.[2]

24. United States Steel
Natural phenol is separated from coal tar at Clairton, PA. Acetone and phenol are produced by cumene peroxidation at Haverhill, OH. Phenol capacity was increased by 90,000 Mg/yr in 1979.[11]

E. REFERENCES*

1. S. A. Cogswell, "Acetone," p 604.5032A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1978).

2. "Chemical Information Services," pp 419 and 420 in 1979 Directory of Chemical Producers, United States of America, SRI International, Menlo Park, CA (1979).

3. Ibid., p 807.

4. S. A. Cogswell, "Acetone," pp 604.5031C-D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1978).

5. "Acetone," p 228 in Chemical Economics Handbook, Manual of Current Indicators ——Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (October 1979).

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8. "Chemical Profile on Phenol," p 9 in Chemical Marketing Reporter (Feb. 6, 1978).

9. "Chemical Profile on Acetone," p 9 in Chemical Marketing Reporter (Nov. 21, 1977).

10. "Chemical Information Services," 1979 Directory of Chemical Producers——Supplement II, SRI International, Menlo Park, CA.

11. J. Beale, Chemical Manufacturers Association, letter dated Nov. 14, 1980, to Robert E. Rosensteel, EPA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

In the United States 97%[1,2] of the phenol is manufactured by the peroxidation of cumene followed by cleavage of the resulting cumene hydroperoxide (CHP).

The two basic reactions of the cumene route to phenol and acetone are as follows:

1. $$\underset{\text{(cumene)}}{C_6H_5CH(CH_3)_2} + \underset{\text{(air)}}{O_2} \longrightarrow \underset{\text{(cumene hydroperoxide)}}{C_6H_5COOH(CH_3)_2}$$

2. $$\underset{\text{(cumene hydroperoxide)}}{C_6H_5COOH(CH_3)_2} \xrightarrow[(H_2SO_4)]{\text{acid}} \underset{\text{(phenol)}}{C_6H_5OH} + \underset{\text{(acetone)}}{CH_3COCH_3}$$

In the peroxidation reaction, as practiced commercially, relatively pure[3] (~99.8%) cumene manufactured on-site or shipped to the site is reacted with oxygen in air in an autocatalytic[4] liquid-phase reaction to form CHP. The reaction is exothermic (about 1000 kJ/kg of cumene[4]). Impurities in the cumene result in increased by-product formation, such as acetaldehyde, methyl ethyl ketone, and propionaldehyde. These by-products are usually[3] vented.

In the second reaction the CHP product of the peroxidation reaction is cleaved to phenol and acetone in the presence of dilute sulfuric acid. The acid promotes this exothermic (about 2700 kJ/kg of phenol) decomposition reaction,[4] which is extremely fast and temperature dependent. After cleavage, the acid in the cleavage product is neutralized and the products and by-products are separated in a series of distillation columns. In addition to the products phenol and acetone, α-methyl styrene and acetophenone are recovered as by-products by some producers.

B. CUMENE PEROXIDATION PROCESSES

At the present time about 47% of the installed phenol capacity using the cumene route is based on process technology licensed by Allied Chemical. The remaining capacity uses processing technology licensed by Hercules (see Table III-1). The major differences between the Allied and Hercules processes involve the

Table III-1. Phenol Plants Using Allied and Hercules Licensed Process Technology

Allied Technology			Hercules Technology		
Plant	Location	1978 Capacity (Gg)	Plant	Location	1978 Capacity (Gg)
Allied Chemical	Frankfort, PA	272	Georgia Pacific	Plaquemine, LA	118
Clark Oil and Refining	Blue Island, IL	40	Monsanto	Chocolate Bayou, TX	227
Dow Chemical	Oyster Creek, TX	211	Shell Oil	Deer Park, TX	227
Getty Oil Co.[a]	El Dorado, KS	43	Standard Oil of California	Richmond, CA	25
Union Carbide	Bound Brook, NJ	82	U. S. Steel Corp.	Haverhill, OH	236[b]
	Penuelas, PR	100	Total		833
Total		748			

[a] Formerly Skelly Oil Company.

[b] 1979 capacity.

operating conditions of the peroxidation reaction and the method of neutralization of the acid in the cleavage product. These differences affect the plant design primarily in the peroxidation and cleavage-product neutralization steps, in the location of process emission points, and in the potential quantity of process emissions.

1. Allied Process

Figure III-1 is a typical flowsheet for the manufacture of phenol and acetone by the Allied process. Cumene (1)* manufactured on-site or shipped to the site and recycle cumene (2) are combined and fed with air to the multiple-reactor system connected in series. The Allied process operates at relatively low temperatures and pressures (compared with those used in the Hercules process) and uses no catalyst or alkaline buffer in the oxidation step.[5] Cooling is required for this exothermic reaction step. Substantial quantities of cumene (5) are carried out of the reactors with the spent air, which contains about 5 vol % O_2. Part of the cumene is recovered and recycled from a refrigerated vent system operated at about 5°C and atmospheric pressure.

The reaction product (6), containing primarily cumene and CHP, is flashed in the CHP concentration column under vacuum to remove most of the cumene, which is recycled. The concentrated CHP (8) flows through the CHP concentrate tank to the cleavage reactor. The cleavage product (10) is neutralized in ion-exchange columns and fed through the crude-product surge tank to a multicolumn distillation system.

The distillation system shown on Fig. III-1 is illustrative of the Allied process[5] and recovers, in addition to phenol and acetone, by-products α-methyl styrene and acetophenone. In the crude-acetone column acetone and lower boiling impurities such as acetaldehyde and formaldehyde are distilled overhead. This product (12) flows through the crude-acetone surge tank to the acetone finishing column, where the acetone is distilled overhead to product quality. Acetone product (14) is accumulated in the acetone day tanks and stored in the acetone storage tank for subsequent loading.

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*Such numbers in parentheses refer to the streams shown on Figs. III-1 and III-2; capital letters refer to emission sources.

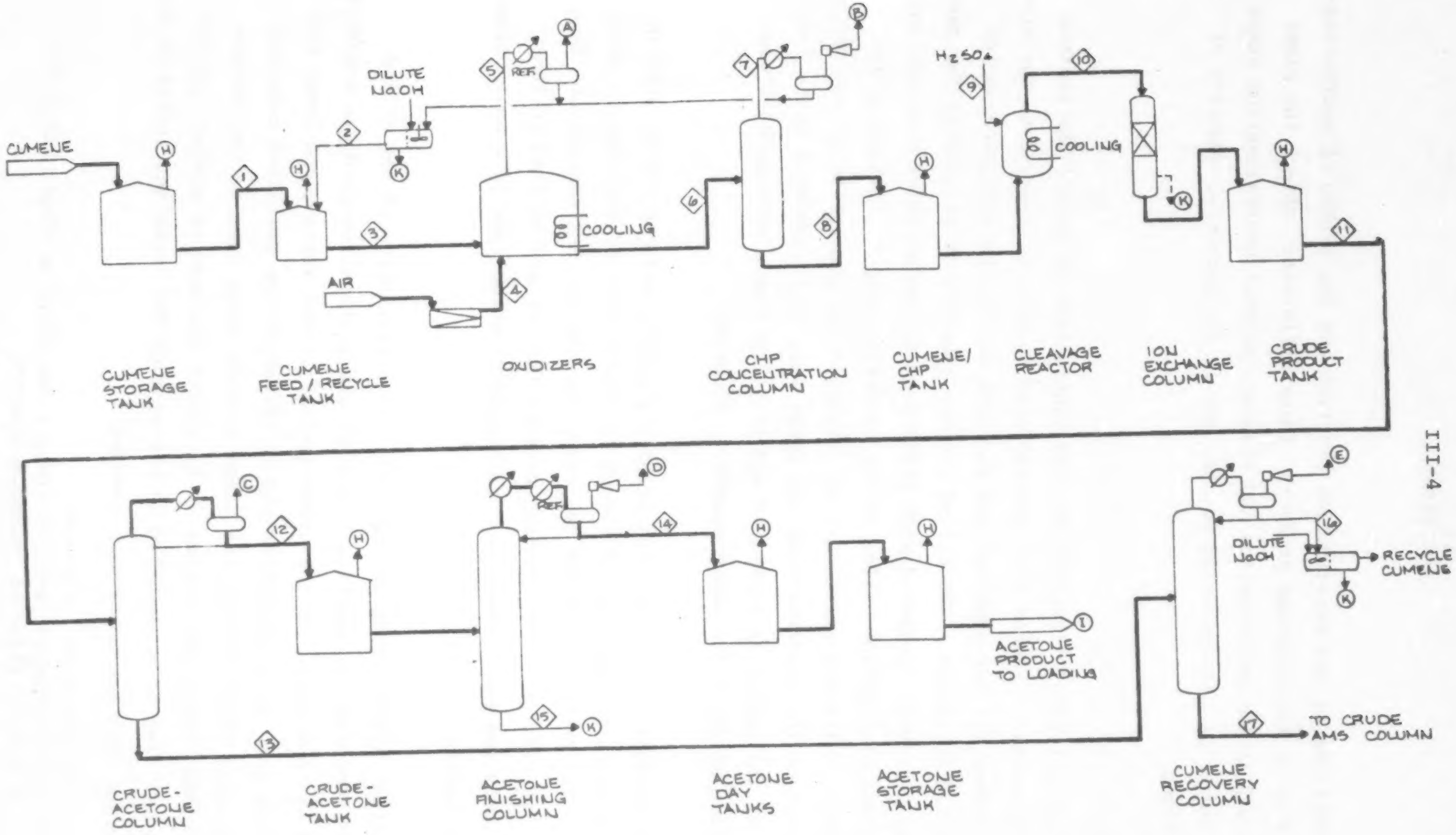
CUMENE
H
1
H
2
DILUTE NaOH
K
3
AIR
4
5
REF.
A
COOLING
6
7
B
8
H
H2SO4
9
COOLING
10
K
H
11
CUMENE STORAGE TANK
CUMENE FEED / RECYCLE TANK
OXIDIZERS
CHP CONCENTRATION COLUMN
CUMENE/ CHP TANK
CLEAVAGE REACTOR
ION EXCHANGE COLUMN
CRUDE PRODUCT TANK
C
12
H
REF.
D
14
H
H
I
ACETONE PRODUCT TO LOADING
15
K
13
E
16
DILUTE NaOH
RECYCLE CUMENE
K
17
TO CRUDE AMS COLUMN
CRUDE-ACETONE COLUMN
CRUDE-ACETONE TANK
ACETONE FINISHING COLUMN
ACETONE DAY TANKS
ACETONE STORAGE TANK
CUMENE RECOVERY COLUMN

Fig. III-1. Flow Diagram for Phenol/Acetone from Cumene Using Allied Technology

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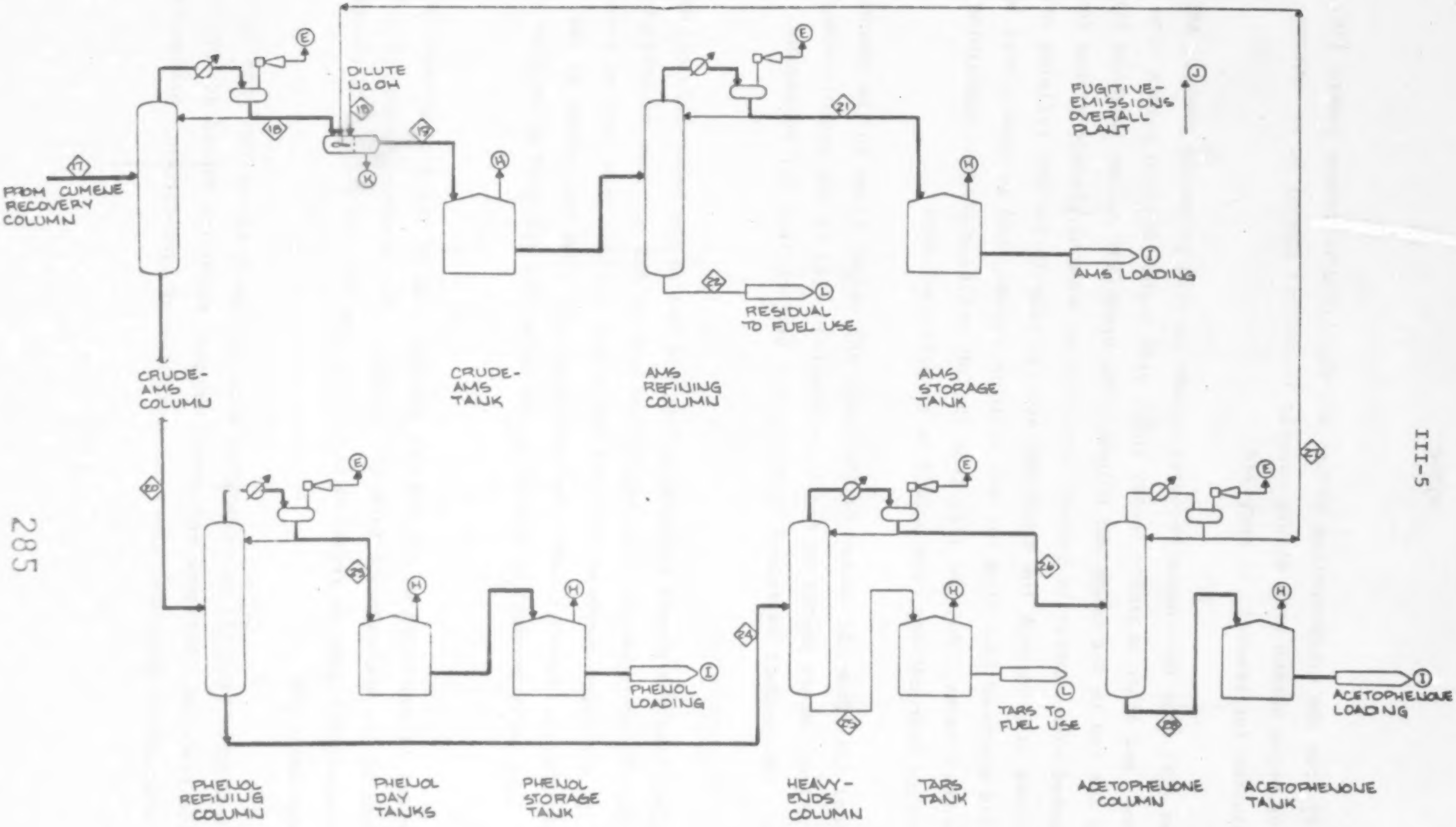
FROM CUMENE RECOVERY COLUMN
17
18
E
DILUTE NaOH
19
K
19
H
21
E
FUGITIVE-EMISSIONS OVERALL PLANT
J
H
AMS LOADING
I
22
L
RESIDUAL TO FUEL USE
CRUDE-AMS COLUMN
CRUDE-AMS TANK
AMS REFINING COLUMN
AMS STORAGE TANK
20
E
23
H
H
PHENOL LOADING
I
24
E
H
25
TARS TO FUEL USE
L
26
27
E
H
28
ACETOPHENONE LOADING
I
PHENOL REFINING COLUMN
PHENOL DAY TANKS
PHENOL STORAGE TANK
HEAVY-ENDS COLUMN
TARS TANK
ACETOPHENONE COLUMN
ACETOPHENONE TANK

Fig. III-1. (Continued).

Page 2 of 2

Bottoms (13) from the crude-acetone column are distilled to remove cumene (16), which, after being washed with dilute caustic to convert phenol to an aqueous phenate solution for removal, is recycled.

The bottoms (17) from the cumene recovery column contain primarily phenol, AMS, acetophenone, and other organics (heavy ends) with higher boiling points than phenol and are fed to the crude-AMS column. The crude-AMS column overhead stream (18) is washed with caustic to convert phenol to an aqueous phenate stream for removal, flows (19) through the crude-AMS storage tank to the AMS refining column, is distilled overhead (21) from the AMS refining column, and is then stored in the AMS product tanks. Bottoms (22) from the AMS refining column, containing higher boiling hydrocarbons, are purged to on-site fuel uses.

Crude phenol (20) from the bottom of the crude-AMS column flows to the phenol refining column, where phenol is distilled overhead (23) to the phenol-product day tanks. The product is stored in the phenol storage tank for subsequent loading.

Bottoms (24) from the phenol refining column are fed to the heavy-ends column, where primarily acetophenone with impurities such as AMS and some dimethylphenyl carbinol is distilled overhead (26) and the higher boiling ends such as para-alpha-cumylphenol, dimers of AMS, and tars exit (25) from the bottom of the column. This tarry product is stored in the tars tank and sold or used as heavy fuel oil.

Acetophenone is separated as the bottoms product (28) of the acetophenone column and stored in the acetophenone tank for loading. The overhead stream (27) from the acetophenone column is recycled to recover the AMS content and to remove the phenol impurity.

The main process vent (A) is associated with the spent-air stream from the air oxidation reaction. Nitrogen and unused oxygen, which are vented at approximately atmospheric pressure, carry out a mixture of hydrocarbons, predominantly cumene.

The second process vent (B) is associated with the vacuum jet on the accumulator of the CHP concentration column. Inert gases, primarily nitrogen, dissolved in the oxidation reaction product (6) are stripped and vented along with cumene, primarily.

The third process vent (C) is associated with the accumulator on the crude-acetone column. Low-boiling hydrocarbons such as acetaldehyde and formaldehyde formed during the two reaction steps are vented, along with some acetone.

The fourth process vent (D) is associated with the acetone finishing column. The VOC in the vent stream is acetone.

The final process vent (E) is associated collectively with the vacuum jets from the remaining six distillation columns in the distillation system. Unreacted ethylbenzene and toluene introduced with the cumene feed, as well as the other VOC products and by-products, are vented. Contaminated wastewater streams (K) result (1) from dilute caustic washes of recycle cumene to remove acidic and phenolic components, which may cause degradation of the product or inhibit the reaction rate in the peroxidation step, (2) from the caustic regeneration of the ion-exchange columns, (3) from wash of the crude-AMS recycle to remove the phenol contaminant as phenate before it is distilled, and (4) from the bottoms from the acetone refining column.

2. Hercules Process

Figure III-2 is a typical flowsheet for the manufacture of phenol and acetone by the Hercules process.

Cumene from storage (1) and recycle cumene (2) are combined and then fed with air (4) to the multiple-reactor system connected in series.[6,7] Additionally, an aqueous Na_2CO_3 solution (3) is fed to the reactor system to promote the peroxidation reaction.[7] This oxidation step is operated at about 95°C and 6.5×10^5 Pa (ref 8). The spent air (5) exiting from the reactors contains about 5 vol % oxygen. Cumene vaporized and flushed from the reactors with the spent air provides cooling for this reaction step. Most of the cumene is recovered and recycled from a refrigerated vent system[8] operated at about 5°C and 5.9×10^5 Pa.

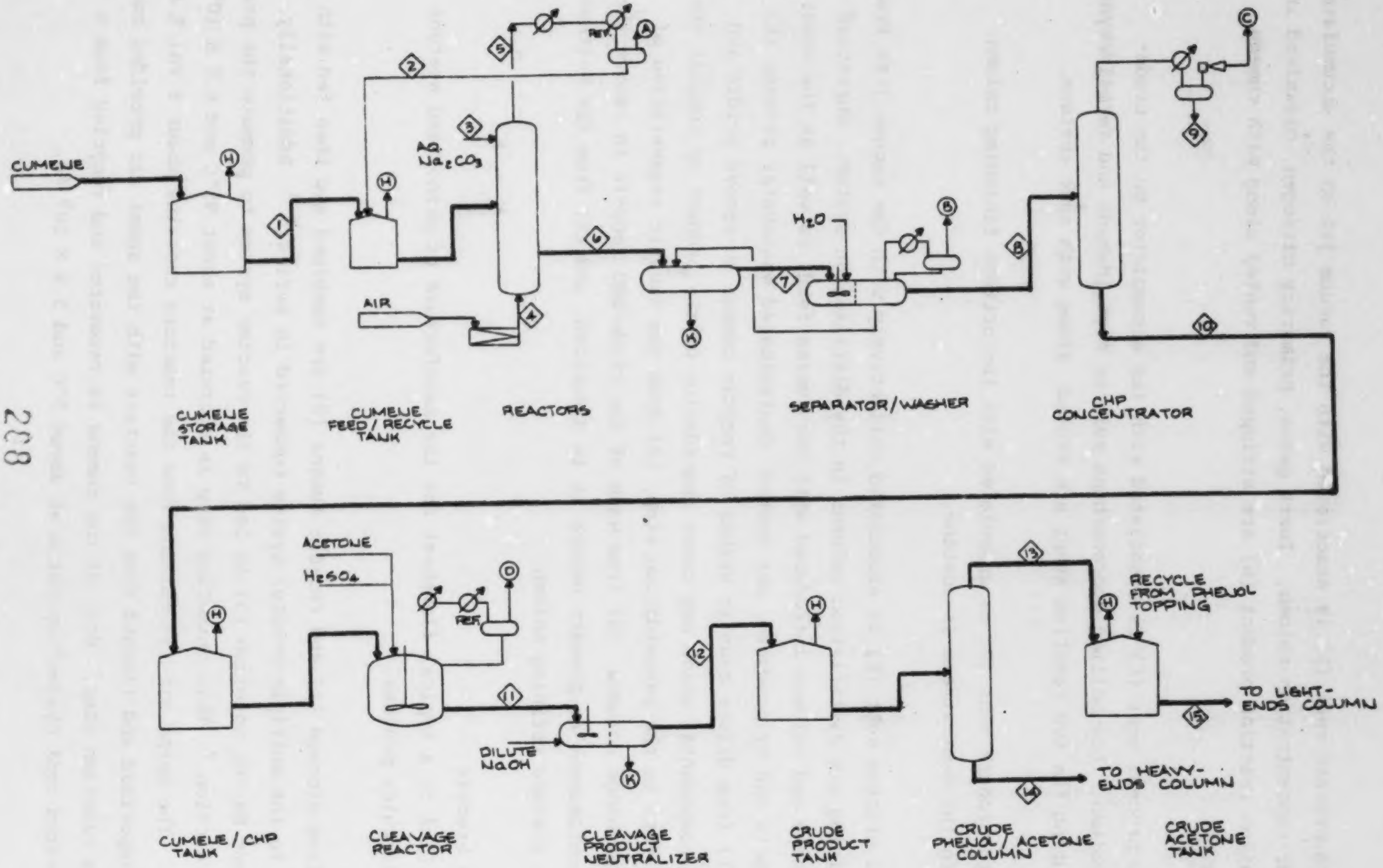
CUMENE
H
1
2
3
AQ. Na_2CO_3
4
AIR
5
REF.
A
6
K
7
H_2O
B
8
9
C
10
CUMENE STORAGE TANK
CUMENE FEED / RECYCLE TANK
REACTORS
SEPARATOR / WASHER
CHP CONCENTRATOR
ACETONE
H_2SO_4
REF.
D
11
DILUTE NaOH
K
12
H
13
RECYCLE FROM PHENOL TOPPING
TO LIGHT-ENDS COLUMN
15
TO HEAVY-ENDS COLUMN
14
CUMENE / CHP TANK
CLEAVAGE REACTOR
CLEAVAGE PRODUCT NEUTRALIZER
CRUDE PRODUCT TANK
CRUDE PHENOL / ACETONE COLUMN
CRUDE ACETONE TANK

Fig. III-2. Flow Diagram for Phenol/Acetone from Cumene Using Hercules Technology

Page 1 of 2

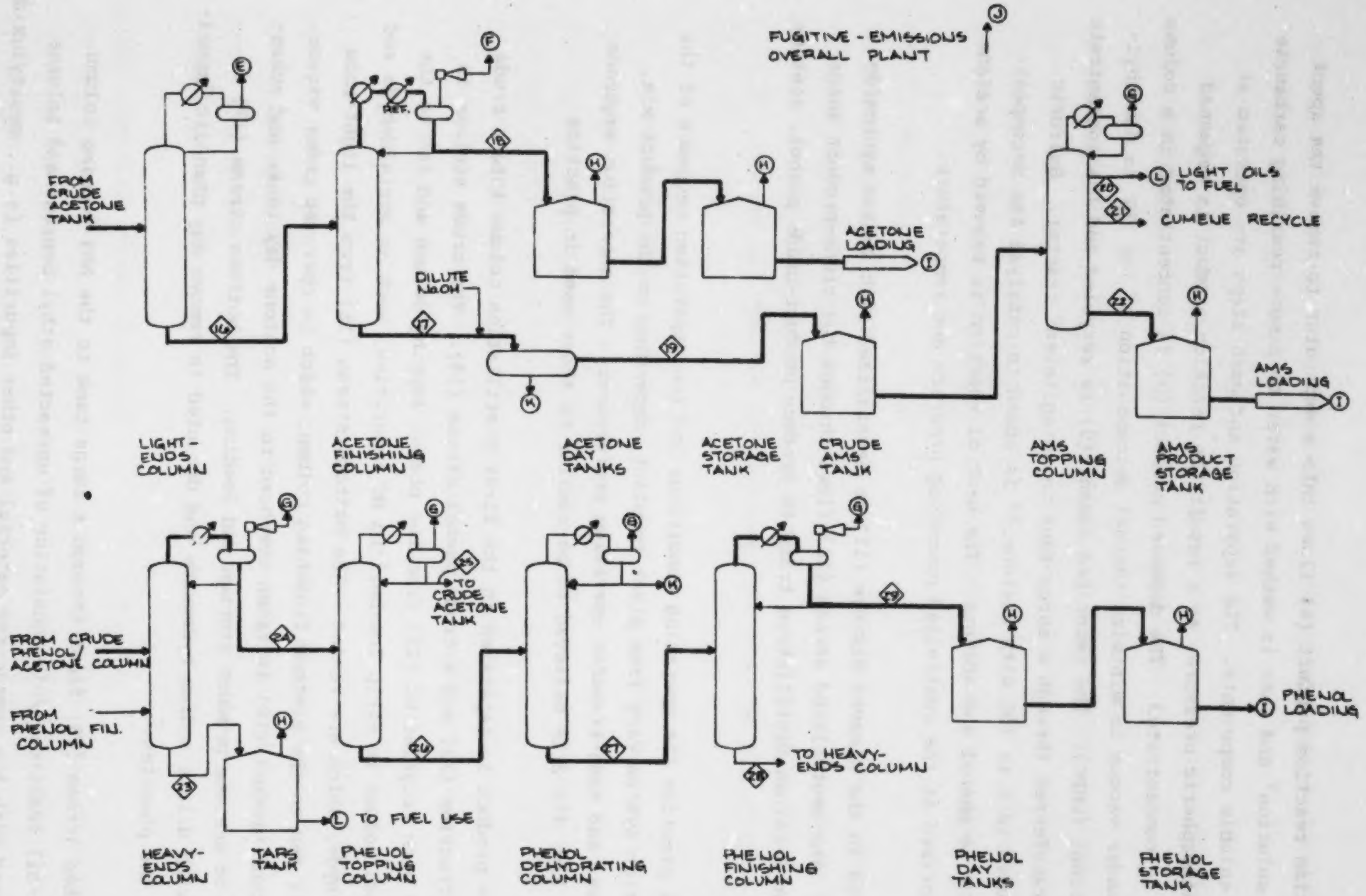
FROM CRUDE ACETONE TANK
E
16
LIGHT-ENDS COLUMN
F
REF.
18
17
DILUTE NaOH
K
ACETONE FINISHING COLUMN
H
H
ACETONE LOADING
I
ACETONE DAY TANKS
ACETONE STORAGE TANK
19
H
CRUDE AMS TANK
FUGITIVE - EMISSIONS OVERALL PLANT
J
G
20
L
LIGHT OILS TO FUEL
21
CUMENE RECYCLE
22
H
AMS LOADING
I
AMS TOPPING COLUMN
AMS PRODUCT STORAGE TANK
FROM CRUDE PHENOL/ACETONE COLUMN
FROM PHENOL FIN. COLUMN
G
23
H
L
TO FUEL USE
HEAVY-ENDS COLUMN
TARS TANK
24
G
25
TO CRUDE ACETONE TANK
26
PHENOL TOPPING COLUMN
B
K
27
PHENOL DEHYDRATING COLUMN
G
28
TO HEAVY-ENDS COLUMN
PHENOL FINISHING COLUMN
29
H
H
I
PHENOL LOADING
PHENOL DAY TANKS
PHENOL STORAGE TANK

Fig. III-2. (Continued)

Page 2 of 2

The oxidation reaction product (6) flows into a separator to remove the spent carbonate solution[7] and then is washed with water to remove remaining carbonate and other soluble components. The separation and wash steps are operated at close to atmospheric pressure; as a result the reaction product is degassed before it is concentrated. The degassed product (8) is concentrated in a column operated under vacuum to minimize thermal decomposition of the CHP to dimethylphenylcarbinol (DMPC). The recovered cumene (9) is recycled and the concentrate (10) is transferred through a surge tank to an agitated[9] reactor. Sulfuric acid, diluted to 5 to 10% with acetone,[10] is added to catalyze the decomposition of CHP to phenol and acetone. The heat of reaction is removed by acetone being vaporized at the controlled operating pressure and temperature.

Excess acid in the cleaved mixture (11) is neutralized with sodium hydroxide solution. The neutralized stream (12) flows through the crude-product surge tank to an 8-column distillation train to produce product-grade phenol, acetone, and AMS.

In actual practice the operating conditions and the separation sequence of the distillation system vary from plant to plant, depending on the product mix, impurities, and mass-transfer operation preferences. The separation sequence shown in Fig. III-2 is believed to be similar to those used in practice.

The crude product is separated in the first distillation column into a crude acetone fraction (13) and a crude phenol stream (14). The crude acetone is combined with recycled HC (25) from the phenol topping column and fed to the light-ends column to strip low-boiling HC impurities, such as acetaldehyde and formaldehyde, which are vented. The bottoms stream (16) from the light-ends column is fed to the acetone finishing column, which is operated under vacuum. The acetone product (18) is taken overhead to the acetone day tanks and subsequently to acetone product storage and loading. The bottoms stream (17) is washed with dilute sodium hydroxide and decanted to remove any phenolic impurities as the phenates.

The washed stream (19) flows through a surge tank to the AMS topping column. A light-oil fraction (20), consisting of unreacted ethyl benzene and toluene introduced with the cumene raw material and other impurities (e.g., mesityloxide), is removed overhead and used on-site for its fuel value. An impure-cumene stream (21) is removed and recycled, and AMS product (22) is transferred to storage.

The crude-phenol stream (14) from the crude phenol/acetone column and the bottoms (28) from the phenol finishing column are fed to the heavy-ends column and distilled under vacuum to separate tars (23) from the impure-phenol stream (24). Hydrocarbons in the tar stream (e.g., cumyl phenols, AMS dimers, acetophenone, DMPC, and phenate[9]) are used as heavy fuel oil for their fuel content[4] (about 37 MJ/kg).

The impure phenol (24) is fed to the phenol topping column to remove hydrocarbons such as cumene and AMS, which remained with the crude phenol stream (14), and AMS formed by dehydration of the DMPC component in the heavy-ends-column feed stream. The phenolic stream (26) is then fed to a dehydrating column, where water is removed overhead as a phenol/water azeotrope.

The dried-phenol stream (27) is distilled under vacuum in the phenol finishing column to separate product-quality phenol (29) from higher boiling components, which are recycled (28).

The main process vent (A) is associated with the spent air stream from the peroxidation reaction following the refrigerated condenser system. Nitrogen, unused oxygen, and a mixture of HC, predominantly cumene, are vented.

Three process vent points (B, C, and D) are associated with the oxidate washer, CHP concentrator, and CHP cleavage reactor. Vents B and C emit cumene primarily, with vent gases desorbed from the oxidation reaction product as the operating pressure is decreased. Vent D emits acetone from the refrigerated condenser on the cleavage reactor.

Another process vent (E) is associated with the accumulator on the light-ends column. Low-boiling hydrocarbons (e.g., acetaldehyde) formed during the two reaction steps are vented, along with some acetone.

Another process vent (F) is associated with the accumulator on the acetone finishing column; the VOC is acetone.

The final process vent (G) is associated collectively with the other five distillation columns and emits a mixture of hydrocarbons.

Contaminated wastewater streams (K) result (1) from separation of the spent carbonate and oxidate wash solution, (2) from dilute caustic washes to neutralize excess cleavage acid and to remove phenolic impurities in the crude-AMS stream, and (3) from water removed in the phenol dehydrating column.

3. Process Variations

There are many possible variations in operating conditions and procedures that will influence the types and quantities of emissions. One example is that the excess oxygen in the spent air can be varied and will directly affect the quantity of spent air and thus the VOC emission rate from the main process vent (A).

Another variation that could greatly reduce the emissions from vent A would be the use of oxygen instead of air in the oxidation step, thereby greatly reducing the inert-gas venting. However, the use of oxygen would increase the explosion hazard and is reportedly[10] not economical. None of the old or newer plants for which detailed process data were secured[5—8] use oxygen instead of air. Both the Allied and Hercules process technologies are based on the use of air in the cumene oxidation step.

Another process variation is the hydrogenation of the crude-AMS stream to produce cumene for recycle rather than to produce an AMS product for sale. This variation would result in a higher yield of phenol and acetone from the cumene raw material and change the emission points and emissions associated with AMS product distillation and storage.

C. OTHER COMMERCIAL PHENOL PROCESSES

The only commercial route to phenol in the United States today other than cumene peroxidation is by toluene oxidation. About 2% of the synthetic phenol is produced by the toluene process. In this process toluene is oxidized, by air in the liquid phase at elevated temperature and pressure (160°C, 5×10^5 Pa) in the presence of cobalt acetate catalyst, to benzoic acid. Following separation, the benzoic acid is catalytically converted to phenol in a liquid-phase oxidative decarboxylation reaction with air at elevated temperature (240°C) and atmospheric pressure.[2]

The only plant producing phenol by benzene sulfonation was reportedly closed and put on standby as of March 1978. This process involves reacting benzene and concentrated sulfuric acid to form benzene sulfonic acid, which is then reacted with sodium sulfite to form sodium benzene sulfonate. The sulfonate is fused with sodium hydroxide to form sodium phenate, which is acidified with sulfur dioxide in the presence of sulfuric acid to form phenol.[2]

D. OTHER COMMERCIAL ACETONE PROCESSES

The only commercial process used in the United States other than the cumene peroxidation route that produces and separates acetone as a product is based on catalytic dehydrogenation of isopropyl alcohol (IPA). In this process IPA is catalytically dehydrogenated to acetone in a vapor-phase reaction at 400 to 500°C.

E. REFERENCES*

1. "No Switch from Cumene, Say Phenol Manufacturers," Chemical Engineering 86(8), 64 (Apr. 9, 1979).

2. S. A. Cogswell, "Phenol," pp 686.5021A— 686.5023J, in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (October 1978).

3. Yen-chen Yen, Report No. 22, Phenol, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (April 1967).

4. P. R. Pujado, J. R. Salazar, and C. V. Berger, "Cheapest Route to Phenol," Hydro-carbon Processing 55(3), 91—96 (1976).

5. C. W. Stuewe, IT Enviroscience, Trip Report for Visit to Allied Chemical Corp., Philadelphia, PA, Mar. 16, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

6. C. W. Stuewe, IT Enviroscience, Trip Report for Visit to Monsanto Chemical Intermediates Co., Alvin, TX, July 28, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

7. C. W. Stuewe, IT Enviroscience, Trip Report for Visit to Georgia Pacific Corp., Plaquemine, LA, Aug. 2, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

8. Shell Oil Co./Shell Chemical Co., Deer Park, TX, Texas Air Control Board Permit Application for Phenol-2 as revised May 9, 1975.

9. Yen-chen Yen, Report No. 22A. Phenol Supplement A, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (September 1972).

10. J. L. Delaney, and T. W. Hughes, Monsanto Research Corp., Source Assessment Manufacture of Acetone and Phenol from Cumene, EPA-600/2-79-019d, (May 1979).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals are photochemically unreactive. However, many photochemically unreactive organic chemicals are of concern and may not be exempt from regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. PROCESS VIA ALLIED TECHNOLOGY

1. Model Plant*

The model plant for the synthesis of phenol and acetone from cumene using Allied Chemical licensed technology has a phenol capacity of 200,000 Mg/yr and an acetone capacity of 120,000 Mg/yr based on 8760 hr** of operation annually. These capacities are typical of recently built or announced plants manufacturing phenol and acetone from cumene. In addition, 10,500 Mg of AMS and 3,750 Mg of acetophenone are recovered annually as by-products. The process shown in Fig. III-1 is believed to be typical of actual processes using Allied technology; however, not all plants recover the AMS and acetophenone by-products.

2. Sources and Emissions

Uncontrolled emission sources and rates are summarized in Table IV-1 and are further described below.

a. Cumene Oxidation——Spent air vented (A, Fig. III-1) from the cumene oxidation reactors following the refrigerated condenser system is the most significant

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*See page I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and the annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Table IV-1. Total Uncontrolled VOC Emissions from a Model Plant Using Allied Technology[a]

Source	Vent Designation (Fig. III-1)	VOC Emission Ratio (g/kg)[b]	VOC Emission Rate (kg/hr)
Cumene oxidation	A	20.630	471.00
CHP concentration	B	1.825	41.67
Crude-acetone (light-ends) column	C	0.300	6.85
Acetone finishing column	D	0.648	14.79
Other distillation column	E	0.060	1.37
Storage vents	H	0.663	15.14
Handling	I	0.250	5.71
Fugitive	J	1.654	37.76
Wastewater treatment	K	0.018	0.41
Incineration of tars	L	0.006	0.13
Total		26.054	594.83

[a] Uncontrolled emissions are emissions from a process for which there are no control devices other than those necessary for economical operation.

[b] g of emissions per kg of phenol produced.

source of VOC emitted from the process. The estimated composition of the uncontrolled vent gas, shown in Table IV-2, is based on reported[1,2] compositions after the use of carbon adsorption for emission control with a reported VOC removal efficiency of 92%.[1]

b. CHP Concentration——The uncontrolled emission from this vacuum distillation step is considered to be the vent stream immediately before the jet aftercondenser. The stream consists primarily of cumene and spent air previously held in solution in the oxidation reaction product plus water vapor from the steam jet. The estimate of the uncontrolled emissions is based on the reported[1] controlled emissions and an estimated control efficiency of 98%.

c. Crude-Acetone, Acetone Finishing, and Other Distillation Columns——Estimates of the emissions from these columns are based on reported rates.[1,3,4] Light hydrocarbons, such as acetaldehyde, generated in the process are vented from the overheads accumulator on the crude-acetone column (vent C, Fig. III-1). Acetone and inert gases are vented from a refrigerated condenser system on the acetone finishing column (vent D, Fig. III-1). Emissions from the other distillation columns (vent E, Fig. III-1) are associated with the vacuum jets on the columns and consist of various hydrocarbons, including predominantly cumene, AMS, and ethylbenzene/toluene.

d. Storage and Handling Emissions——Emissions result from feed, intermediate-product, and final-product storage tanks. Sources are described in Table IV-3 and shown as vent H on Fig. III-1. Storage tank data were calculated by use of equations from AP-42[5] based on fixed-roof tanks, half full, with a diurnal temperature variation of 11°C. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overpredicts emissions.[6] Handling emissions result from the loading (vent I, Fig. III-1) of acetone and phenol into tank cars and tank trucks for shipment. Handling emissions are shown in Table IV-1 and were calculated with the equations from AP-42,[5] based on submerged loading of tank cars and tank trucks, with phenol at 49°C and all other products at 27°C. Emissions from the loading of AMS and acetophenone are insignificant (44×10^{-6} g/kg and 2×10^{-6} g/kg respectively). Acetone accounts for two-thirds of the total VOC in the storage emissions and for over 95% of the VOC in the handling emissions.

Table IV-2. Estimated Composition of Oxidation Vent Gas from Model Plant Using Allied Technology[a]

Component	Composition (wt %)
Cumene	0.92
Other VOC	0.23
Total VOC	1.15
Spent air (O_2, N_2, CO_2)	98.85
Total	100.00

[a] See refs 1 and 2.

Table IV-3. Storage Requirements for 200,000-Mg/yr Model Plant Using Allied Technology

Stored Material	Number of Tanks	Tank Size (M gal)	Turnovers Per Year	Bulk Liquid Temperature (°F)
Cumene	1	3000	23	80
Cumene feed/recycle	1	1000	6[a]	80
Cumene/CHP	1	1000	6[a]	160
Crude product	1	300	6[a]	110
Crude acetone	1	100	6[a]	80
Acetone (day)	2	150	133	80
Acetone product	1	300	133	80
Crude AMS	1	20	6[a]	80
AMS product	2	100	15	80
Phenol (day)	2	150	163	120
Phenol product	1	3000	16	120
Tars	1	10	204	200
Acetophenone	1	20	48	85

[a] Surge tanks with nearly constant level.

e. Fugitive Emissions—Process pumps, process valves, and pressure-relief valves are potential sources (J) of fugitive emissions. The model plant is estimated to have 148 pumps, 998 process valves, and 54 relief valves, based on data supplied by a producer.[7] The fugitive emission factors from Appendix B were applied to these estimates; the results are shown in Table IV-1.

f. Secondary Emissions—Emissions can result from handling and disposal of process waste streams. For the model plant, sources of wastewater and tars or residuals (K,L) are indicated on Fig. III-1.

Estimates of the secondary emissions from wastewater treatment are based on reported[1,3] flows and organic contents of phenolic and nonphenolic wastewater. Emissions from wastewater will be discussed in an EPA report[8] on secondary emissions.

The cumene process forms substantial quantities of tarry products that can be used as fuel or can be disposed of by incineration.[9—11] The venting of flue gas from combustion of these waste products results in secondary emissions of VOC. Emissions from such sources are characteristically low. An emissions estimate was based on AP-42,[12] with the tars assumed to be similar to residual oil in industrial and commercial boiler service.

B. PROCESS BY HERCULES TECHNOLOGY

1. Model Plant

The model plant for the synthesis of phenol and acetone from cumene using Hercules licensed technology has the same product capacity as the model plant representing Allied technology; however, the by-product mix is different. The capacities are respectively 200,000, 120,000, and 10,500 Mg/year for phenol, acetone, and AMS based on 8760 hr of operation annually. Acetophenone is not recovered as a by-product but remains with the waste tars from the process. This capacity is typical of recently built or announced plants manufacturing phenol and acetone from cumene. The process depicted in Fig. III-2 is believed to be typical of actual processes using Hercules technology.

2. Sources and Emissions

Uncontrolled emission sources and emission rates are summarized in Table IV-4 and described in greater detail below.

a. Cumene Oxidation——The largest source of VOC emitted from this process is the spent air vented from the cumene oxidation reactors (vent A, Fig. III-2) following the refrigerated condenser system. The composition of the uncontrolled vent gas, shown in Table IV-5, is based on reported[3] data. It should be noted that the order-of-magnitude difference in uncontrolled emissions from this step as shown in Tables IV-1 and IV-4 for Allied and Hercules technology respectively is due to the comparatively high operating pressure for the refrigerated condenser system in the Hercules process.

b. Oxidate Wash and Separation——Estimates of this source (vent B, Fig. III-2) are for the vent stream following partial recovery of VOC using a water-cooled condenser. The estimate is based on the estimated release of inert gases from the oxidate stream as the system pressure is reduced. The vent emission consists primarily of cumene and spent air.

c. CHP Concentration——The uncontrolled emissions from this vacuum distillation step is the vent stream from the accumulator immediately before the jet after-condenser (Vent C, Fig. III-2). The stream consists primarily of cumene, spent air, and water vapor from the steam jet. The uncontrolled emissions estimate is based on an estimate of the solubility of inert gases in the oxidate stream prior to distillation.

d. CHP Cleavage——This source of uncontrolled emissions (vent D, Fig. III-2) is determined at a point immediately following the refrigerated condenser. The emitted VOC is primarily acetone. The emission estimate is based on reported[3] data.

e. Light-Ends, Acetone Finishing, and Other Distillation Columns——Estimates of the emissions from the various distillation columns are based on reported rates.[1,3,4,7] The light-ends source (vent E, Fig. III-2) consists of light hydrocarbons such as acetaldehyde that are generated in the process. These light hydrocarbons are purged from the process, along with acetone, from the

Table IV-4. Total Uncontrolled VOC Emissions from a Model Plant Using Hercules Technology[a]

Source	Vent Designation (Fig. III-1)	VOC Emission Ratio (g/kg)[b]	VOC Emission Rate (kg/hr)
Cumene oxidation	A	2.314	52.83
Oxidate wash/separation	B	0.078	1.79
CHP concentration	C	1.217	27.78
CHP cleavage	D	0.473	10.80
Light-ends column	E	0.300	6.85
Acetone finishing column	F	0.648	14.79
Other distillation column	G	0.060	1.37
Storage vents	H	0.660	15.06
Handling	I	0.249	5.70
Fugitive	J	1.654	37.76
Secondary			
Wastewater treatment	K	0.027	0.62
Incineration of tars	L	0.008	0.17
Total		7.688	175.52

[a] Uncontrolled emissions are emissions from a process for which there are no control devices other than those necessary for economical operation.

[b] g of emissions per kg of phenol produced.

Table IV-5. Estimated Composition of Oxidation Vent Gas from Model Plant Using Hercules Technology[a]

Component	Composition (wt %)
Cumene	0.12
Other VOC	0.01
Total VOC	0.13
Spent air (O_2, N_2, CO_2)	99.78
H_2O	0.09
Total	100.00

[a] See ref 3.

overhead accumulator on the column. The vent from the refrigerated condenser on the acetone finishing column (vent F, Fig. III-2) emits acetone and inert gases. Vents from the other distillation columns (vents G, Fig. III-2) are associated with the accumulators, vacuum jets, and condensers on the columns and contain various hydrocarbons, including, predominantly, cumene, AMS, and ethyl benzene.

f. Storage and Handling Emissions——Emissions result from feed, intermediate-product, and final-product storage tanks. Sources are shown as vents H in Fig. III-2 and are further described in Table IV-6. Equations from AP-42[5] were used for calculating storage-tank data based on fixed-roof tanks, operated half full, and experiencing a diurnal temperature variation of 11°C. The resulting breathing-loss data were divided by 4 to account for recent evidence indicating that the AP-42 breathing-loss equation overpredicts emissions.[6] Loading acetone and phenol into tank cars and tank trucks for shipment results in handling-emission sources (vent I, Fig. III-2). These emissions are shown in Table IV-4 and were calculated with the equations from AP-42,[5] based on submerged loading in tank cars and tank trucks, with phenol at 49°C and all other products at 27°C. Acetone accounts for about two-thirds of the total VOC in the storage emissions and over 95% of the VOC in the handling emissions. Emissions from loading AMS are insignificant (44×10^{-6} g/kg of phenol produced).

g. Fugitive Emissions——The estimate and bases are the same as those used for the Allied technology model plant discussed in Sect. IV-A-2e. The sources are identified as vent J in Fig. III-2.

h. Secondary Emissions——Sources of emissions (vents K and L, Fig. III-2) are wastewater and tars or residuals. The bases and discussion in Sect. IV-A-2f also apply to the Hercules model plant. In addition to phenolic and non-phenolic wastewater streams similar to those in the Allied technology, the Hercules process generates a spent aqueous Na_2CO_3 stream containing VOC, primarily cumene. The secondary-emission estimate in Table IV-4 includes an estimate for this added source.

Table IV-6. Storage Requirements for 200,000-Mg/yr Model Plant Using Hercules Technology

Stored Material	Number of Tanks	Tank Size (M gal)	Turnovers Per Year	Bulk Liquid Temperature (°F)
Cumene	1	3000	23	80
Cumene feed/recycle	1	1000	6[a]	80
Cumene/CHP	1	1000	6[a]	160
Crude product	1	300	6[a]	110
Crude acetone	1	100	6[a]	80
Acetone (day)	2	150	133	80
Acetone product	1	300	133	80
Crude AMS	1	20	6[a]	80
AMS product	2	100	15	80
Phenol (day)	2	150	163	120
Phenol product	1	3000	16	120
Tars	1	20	165	200

[a] Surge tanks with nearly constant level.

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V. APPLICABLE CONTROL SYSTEMS

A. PROCESS VIA ALLIED TECHNOLOGY

Applicable control systems and emission estimates are summarized in Table V-1 and discussed below.

1. Cumene Oxidation

In the Allied process 88% of the uncontrolled process emissions come from vent A (Fig. III-1). The control option selected for the model-plant cumene oxidation vent is carbon adsorption. With good design and operation the VOC content in the vent from the carbon adsorption unit is estimated to fall in the range of 50 to 100 ppm_v, with 0.3 kg of steam/kg of carbon used for regeneration. The resulting VOC emission reduction is 97.5% at an expected 70 ppm_v. At 100 ppm_v, VOC emission reduction would be 96.4%. The design is based on a 0.91-m-deep bed, a superficial velocity of 0.51 m/s, and an estimated loading capacity of 11 lb of VOC/100 lb of carbon (see the report[1] on carbon adsorption). Potential alternative controls for this emission source include the use of other adsorbents (e.g., resins).[2]

The regeneration cycle operation can have a significant effect on the VOC content in the vent. With operation at a regeneration steam ratio of 1 kg of steam/kg of carbon it is estimated that the VOC content in the vent would fall in the range of 5 to 20 ppm_v. At an expected 12 ppm_v the VOC emission reduction would be 99.6%; at 20 ppm_v it would be 99.3%.

2. CHP Concentration

The primary VOC in vent B (Fig. III-1) is cumene. Condensation at 4.4°C and atmospheric pressure was selected as the control option. Vacuum conditions on this distillation column are maintained by use of a steam-jet and condenser system. Use of the refrigerated condenser after the jet condenser is particularly effective, due to both the overall increased system pressure and the reduced temperature, in decreasing the VOC in the vent. The overall VOC reduction is estimated to be greater than 98%. An EPA report[3] will cover condensation as a control option.

Table V-1. Estimates of Controlled VOC Emissions from a Model Plant Based on Allied Technology

Source	Vent Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emission	
				Ratio (g/kg)[a]	Rate (kg/hr)
Cumene oxidation	A	Carbon adsorption[b]	97.5	0.523	11.94
CHP concentration	B	Refrigerated condenser	98	0.036	0.83
Light-ends column	C	Combustion in boiler	~100	$\sim 1 \times 10^{-4}$	$\sim 2 \times 10^{-3}$
Acetone finishing column	D	Vent scrubber	96	0.026	0.59
Other distillation columns	E	No controls identified		0.060	1.37
Storage and handling	H, I	Vent scrubber on acetone emitting vents	76	0.222	5.07
Fugitive	J	Detection and correction of major leaks	71	0.478	10.92
Secondary					
Wastewater treatment	K	None		0.018	0.41
Incineration of tars and residuals	L	None		0.006	0.13
Total				1.369	31.26

[a] g of emission per kg of phenol produced.

[b] Regeneration with 0.3 lb of steam/lb of carbon.

3. Light-Ends Vent

This vent stream is rich in acetone, aldehydes, and other combustible hydrocarbons. The control option selected for the light-ends vent is combustion in an existing boiler or incinerator. Based on emission factors from AP-42[4] the VOC reduction is estimated to be almost 100%. Installation of an incinerator solely for the purpose of controlling this source would not be justifiable; therefore this control method is applicable only if an existing combustion chamber can be used. This vent stream is flammable, and safe handling practices should be considered in the design and operation of the collection and transport system.

Another option used for control of the VOC in this vent stream is aqueous scrubbing.[5] It is estimated that a VOC reduction of 96 to 98% could easily be obtained since the major VOC constituents are highly soluble in water. A potential disadvantage of aqueous scrubbing is that part of the VOC removed may be emitted as secondary emissions during wastewater treatment. Treatment of the scrubbing liquor in an acetone recovery system before it is sent to wastewater treatment would result in recovery of other light hydrocarbons and defeat the purpose of the light-hydrocarbon (light ends) stripping in the crude-acetone column.

4. Acetone Finishing Column

The VOC in this vent should be relatively pure acetone and thus recoverable. Aqueous scrubbing of the acetone finishing column vent was selected as the control option. A slightly reduced pressure in this column is maintained with a steam-jet and condenser system to enhance separation efficiencies. The scrubber would be applied to the vent from the jet after-condenser. It is estimated that the overall VOC emission reduction would be 96%. A future EPA report[6] will discuss the use of absorption as a control option.

An alternative control option could be chilled condensation. It is estimated that the overall VOC emission reduction would be only about 40% based on the physical properties of the vent stream at condensation conditions of 4.4°C and atmospheric pressure.

5. Other Distillation Columns

The VOC in the emissions from the other distillation columns contain phenol, cumene, AMS, and other hydrocarbons. Since the emission level is relatively low, no control options were identified for the model plant.

6. Storage and Handling

The major component of the VOC in the vents from storage and from handling, particularly, is acetone. The control option selected for the model-plant storage and handling sources is aqueous scrubbing on the acetone emitting vents. These vents include acetone loading, acetone day tanks, acetone product tank, crude-product tank, and crude-acetone tank. A conservative estimate of 96% VOC removal efficiency was used to calculate the reduction of VOC in these vents, resulting in an overall VOC emission reduction of 76%.

Floating-roof tanks have been reported as a control option on acetone tanks.[5,7,8] The controlled storage emissions on the acetone tanks were calculated by assuming that a contact type of internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85%.[9] With this control on only the acetone emitting tanks the overall reduction will be 45%. Another EPA report[10] covers control options for storage and handling.

7. Fugitive

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry will be discussed in a future EPA document.[11] Emissions from pumps and valves can be controlled by appropriate leak-detection systems, repairs, and maintenance as required. Controlled fugitive emissions calculated with the factors given in Appendix B are included in Table V-1; these factors are based on the assumption that major leaks are detected and corrected.

8. Secondary Emissions

No additional control systems for secondary emissions have been identified for the model plant. An EPA report[12] discusses control of secondary emissions.

B. PROCESS BY HERCULES TECHNOLOGY

A summary of applicable control systems and emission estimates is given in Table V-2 and discussed below.

Table V-2. Estimates of Controlled VOC Emissions from a Model Plant Based on Hercules Technology

Source	Vent Designation (Fig. III-3)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emission Ratio (g/kg)[a]	VOC Emission Rate (kg/hr)
Cumene oxidation	A	Carbon adsorption[b]	77.4	0.523	11.94
Oxidate wash separation	B	Refrigerated condenser	86	0.011	0.25
CHP concentration	C	Refrigerated condenser	98	0.024	0.56
CHP cleavage	D	Vent scrubber	96	0.019	0.43
Light-ends column	E	Combustion in boiler	∿100	$\sim 1 \times 10^{-4}$	$\sim 2 \times 40^{-3}$
Acetone finishing column	F	Vent scrubber	96	0.026	0.59
Other distillation columns	G	No controls identified		0.060	1.37
Storage and handling	H, I	Vent scrubber on acetone emitting vents	76	0.218	4.98
Fugitive	J	Detection and correction of major leaks	71	0.478	10.92
Secondary					
Wastewater treatment	K	None		0.027	0.62
Incineration of tars and residuals	L	None		0.008	0.17
Total				1.394	31.83

1. Cumene Oxidation

In the Hercules process 45% of the uncontrolled process emissions emanate from the cumene oxidation vent source (vent A, Fig. III-2). For the model plant, carbon adsorption was selected as the control option for the cumene oxidation vent. With proper design and operation the VOC content in the vent from the carbon adsorption unit should be within a range of 50 and 100 ppm_v, with 0.3 kg of steam/kg of carbon used for regeneration. The resulting VOC emission reduction is 77.4% at the expected 70 ppm_v. In the Hercules process the vent stream exiting from the refrigerated condenser at 4 to 5°C and 5.9×10^5 Pa can be cross-exchanged with the hot vent stream from the reactors both to recover heat and, more importantly, to decrease the relative humidity of the water vapor in the gas stream. At high relative-saturation pressures, water vapor will compete with the organic vapors for the carbon's adsorptive capacity.[13] The system design is based on a 0.91-m-deep bed, a superficial velocity of 0.51 m/s, and a loading factor calculated by the method given in an EPA report[1] on carbon adsorption.

At a regeneration steam ratio of 1 kg of stream/kg of carbon the VOC content in the vent is estimated to fall between 5 and 20 ppm_v. At an expected 12 ppm_v the VOC emission reduction would be 96.1%.

2. Oxidate Wash/Separation

This relatively small source of VOC (vent B, Fig. III-2) consists primarily of cumene with inert gases. The control option selected for this source is condensation by use of a refrigerated coolant. The estimate of controlled emissions is based on physical properties for the estimated stream composition at the condensing conditions of 4.4°C and atmospheric pressure. The estimated emission reduction is 86%. A future EPA report[3] will cover condensation as a control device.

3. CHP Concentration

The control-option selection and discussion in Sect. V-A-2 for the Allied process is directly applicable to this vent in the Hercules process.

4. CHP Cleavage

The VOC in this vent stream is primarily acetone. Economical operation requires partial condensation of acetone vapor by use of a refrigerated coolant as part of the process. The control option selected for the CHP cleavage vent is aqueous scrubbing and would be applied to the vent from the refrigerated condenser. It is estimated that the overall VOC emission reduction would be 96%. Another EPA report[6] will further discuss absorption as a control option.

5. Light-Ends Column Vent

Although the distillation sequence differs for the Allied and Hercules model plants, the light-ends vent stream is similar for the two processes. The same control-option selection and discussion given in Sect. V-A-3 for the Allied process are applicable to this source (vent E, Fig. III-2) for the Hercules process.

6. Acetone Finishing Column

The control-option selection and discussion in Sect. V-A-4 for the Allied process are applicable for this source (vent F, Fig. III-2) for the Hercules process.

7. Other Distillation Columns

Since the emission level is relatively low, no control options were identified for this source (vent G, Fig. III-2) for the Hercules model plant.

8. Storage and Handling

The control-option selection and discussion in Sect. V-A-6 for the Allied model plant are applicable for these sources (vents H and I, Fig. III-2) for the Hercules model plant.

9. Fugitive

This source (vent J, Fig. III-2) can be controlled in the manner that is discussed for the Allied model plant in Sect. V-A-7.

10. Secondary Emissions

No additional controls were identified for this source (vents K and L, Fig. III-2).

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9. W. T. Moody, TRW, Inc., letter dated Aug. 15, 1979, to David A Beck, EPA, ESED, Research Triangle Park, NC.

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VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Process by Allied Technology

Table VI-1 gives the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices or techniques results in an estimated reduction of total VOC emissions by 94.8%, or about 4940 Mg/yr for the model plant, resulting in controlled emissions from the model plant of about 270 Mg/yr.

a. Cumene Oxidation Vent——The adsorption with carbon of VOC from the spent air from the oxidation reactors reduces the model-plant VOC emissions by 4021 Mg/yr. Adsorbed VOC is recovered and then recycled as process feed. The major energy impact results from the required regeneration steam, which is estimated to be equivalent to about 6000 MJ/Mg of VOC removed.

b. All Other Process Vents——The control of vent sources B, C, and D by the control options shown in Table VI-1 reduces the model-plant VOC emissions by 541 Mg/yr. The energy for these controls is impacted by the required refrigeration for the condenser coolant and the energy required to either recover the acetone from the scrubber effluent or destroy the acetone in a biological wastewater treatment system. These energy requirements are offset by the potential heat recovery from combustion of the light ends in an existing boiler. The overall energy impact is estimated to be a net credit of about 86 MJ/hr. The impact ratio is estimated to be a credit of about 1380 MJ/Mg of VOC removed.

c. Nonprocess Emissions (Storage, Handling, and Fugitive)——Storage and handling emissions from the model plant are partly controlled by aqueous scrubbing of the acetone emitting tanks and the acetone loading vents. Application of this control results in a VOC emission reduction of 138 Mg/yr for the model plant. Fugitive emissions are controlled by the repair of leaking components. VOC emissions reduction by control of fugitive emissions is estimated to be 235 Mg/yr. A separate EPA report[1] covers energy requirements for the control of storage and handling emissions.

Table VI-1. Environmental Impact of Controlled Model Plant Using Allied Technology

	Vent		VOC Emission Reduction	
Emission Source	Designation (Fig. III-1)	Control Device or Technique	(%)	(Mg/yr)
Cumene oxidation	A	Carbon adsorption	97.5	4021
CHP concentration	B	Refrigerated condenser	98	358
Crude-acetone (light-ends) column	C	Combustion in existing boiler	~100	60
Acetone finishing column	D	Vent scrubber	96	124
Other distillation column	E	None		
Storage and handling vents	H, I	Vent scrubber on acetone emitting vents	76	138
Fugitive	J	Detection and correction of major leaks	71	235
Secondary				
Wastewater treatment	K	None		
Incineration of tars	L	None		
Total				4936

2. Process by Hercules Technology

Table VI-2 summarizes the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices results in an estimated reduction in total VOC emissions by 82%, or about 1260 Mg/yr, and results in controlled emissions from the model plant of about 275 Mg/yr.

a. Cumene Oxidation Vent——Application of carbon adsorption to the spent air from the oxidation reactors reduces model-plant VOC emissions by 358 Mg/yr. The adsorbed VOC is recovered and then recycled to the process. The main energy impact results from the steam required for regeneration of the carbon. The energy equivalent of the steam is estimated to be about 11 GJ/Mg of VOC removed.

b. All Other Process Vents——Control of vent sources B—F by the control options shown in Table VI-2 reduces the model-plant VOC emissions by 529 Mg/yr. Energy for these controls is impacted by the required refrigeration for the condenser coolants and the energy required to either recover the acetone from the scrubber effluent or destroy the acetone in a biological wastewater treatment system. These energy requirements are partly offset by the potential heat recovery from combustion of the light ends in an existing boiler. The overall energy impact is estimated to be a net requirement of about 4 MJ/hr. The impact ratio is estimated to be about 66 MJ/Mg of VOC removed.

c. Nonprocess Emissions (Storage, Handling, and Fugitive)——Emissions from the model-plant storage and handling are partly controlled by aqueous scrubbing of the acetone emitting tanks and the acetone loading vents. The estimated VOC emission reduction for the model plant through application of this control is 138 Mg/yr. Fugitive emissions are controlled by the repair of leaking components, with an estimated VOC emission reduction of 235 Mg/yr. A separate EPA report[1] covers energy requirements for the control of storage and handling emissions.

3. 1980 Industry Emissions

The total VOC emissions from the domestic production of phenol/acetone by the cumene process are estimated at 4030 Mg and include estimated emissions from the process, fugitive, secondary, and storage and handling sources. This

Table VI-2. Environmental Impact of Controlled Model Plant Using Hercules Technology

Emission Source	Vent Designation (Fig. III-2)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)
Cumene oxidation	A	Carbon adsorption	77.4	358
Oxidate wash/separation	B	Refrigerated condenser	86	13
CHP concentration	C	Refrigerated condenser	98	238
CHP cleavage	D	Vent Scrubber	96	91
Light-ends column	E	Combustion in boiler	~100	60
Acetone finishing column	F	Vent scrubber	96	124
Other distillation column	G	None		
Storage and handling vents	H, I	Vent scrubber on acetone emitting vents	76	138
Fugitive	J	Detection and correction of major leaks	71	235
Secondary				
Wastewater treatment	K	None		
Incineration of tars	L	None		
Total				1257

estimate is based on a projected 1980 level of production of 1,320,000 Mg. The estimated emissions were determined by applying the emission ratios from Tables IV-1, IV-4, V-1, and V-2. Process emissions are estimated to be 92% controlled, storage and handling emissions to be 67% controlled, and fugitive emissions to be uncontrolled. Emissions from secondary sources are believed to be negligible. Controls reported by producers are summarized in Appendix C.

B. COST CONTROL IMPACT

The cost control impact described below relates to the production of phenol/acetone by the cumene process by Allied and Hercules technology. Details of the model plants (Figs. III-1 and 2) are given in Sects. III and IV.

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of production lost during installation or startup, research and development, or land acquisition. If retrofitting is considered for these controls, it should be recognized that a primary difficulty in retrofitting may be in finding space to fit the control system into the existing plant layout. Because of these associated costs the cost of retrofitting emission control systems in existing plants may be appreciably greater than that for a new installation.

Bases for the annual cost estimates for the control alternatives include utilities, raw materials, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. (Incremental operating labor costs are assumed to be minimal and therefore are not included.) Emission recovery credits are based on the raw-material value of the material recovered.[2] Annual costs are for a 1-year period beginning mid-1979.

1. Cumene Oxidation Emissions

The major source of emissions from the production of phenol/acetone by the cumene process for both Allied and Hercules technology is the spent air from the cumene oxidation reaction. These emissions are controlled by a carbon adsorption system. The cost estimate for the control system is based on a separate EPA report on carbon adsorption as a control option.[3] As applied to the Hercules model plant the carbon adsorption system does not require a vent stream blower. Capital and operating costs were adjusted to reflect this change. The costs and cost effectiveness are summarized in Table VI-3 at two regeneration steam ratios: 0.3 and 1.0 kg of steam/kg of carbon. The VOC emission reduction given in Tables VI-1 and VI-2 are based on a regeneration steam ratio of 0.3 kg of steam/kg of carbon. The VOC emission reduction benefit resulting from use of the higher steam ratio is discussed in Sects. V-A-1 and V-B-1.

2. Other Process Emissions

Emissions from other process vents are controlled as shown in Tables VI-1 and VI-2 by condensation, combustion, and absorption (vent scrubbing). Condensation and absorption are covered in separate EPA reports.[4,5] The predominant cost involved in the use of an existing boiler or incinerator would be installation of the piping necessary to transfer the vent stream to the combustion device. As the cost of the required piping will depend primarily on the distance of the phenol/acetone plant from the combustion device, which can vary greatly, the cost impact was not determined. Another EPA report[6] covers the use of emissions as fuel.

3. Storage and Handling Sources

The control method for storage and handling is aqueous scrubbing of the acetone emitting vents. Another EPA report[1] covers applicable controls for storage and handling emissions.

4. Fugitive Sources

A future EPA document[7] will cover fugitive emissions and applicable controls.

5. Secondary Sources

No control system has been identified for controlling the secondary emissions from wastewater treatment or from the disposal of residues by incineration. An EPA document[8] covers secondary emissions for the synthetic organic chemicals manufacturing industry.

Table VI-3. Summary of Costs and Cost Effectiveness for Carbon Adsorption Applied to Allied and Hercules Model Plants

Technology	Regeneration Steam Ratio (kg of steam/kg of carbon)	Costs				Cost Effectiveness (per Mg removed)
		Installed Capital	Annual	Annual Recovery Credit	Net Annual	
Allied	0.3	$574,000	$259,000	$1,443,000	($1,184,000)[a]	($294)[a]
	1.0	574,000	434,000	1,469,000	(1,035,000)[a]	(252)[a]
Hercules	0.3	$517,000	$177,000	$120,000	$57,000	$156
	1.0	517,000	200,000	147,000	53,000	119

[a] Savings.

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VII. SUMMARY

Phenol and acetone are co-products of the cumene peroxidation process, which accounts for about 97%[1,2] of the phenol manufactured in the United States. As of 1978 the cumene process also accounted for about 67% of the domestic acetone production.[3] At projected annual growth rates of 4.5%[4] for phenol and 4 to 5%[5] for acetone, production will reach about 87% and 77 to 81% of current capacity by 1982 for phenol and acetone respectively.

Two process variations of the basic cumene peroxidation route are practiced commercially. About 47% of the current capacity utilizes a process based on Allied Chemical licensed technology. The remaining capacity is based on Hercules licensed technology.

Emission sources and uncontrolled and controlled emission rates for the model plants based on the two processes are given in Tables VII-1 and VII-2. The most significant process emission sources of both processes are the cumene oxidation reaction vents, which are controlled in the model plants by carbon adsorption.

Storage and handling emissions are predominantly acetone. These emissions for the model plants are controlled by aqueous scrubbing. Potential secondary emissions are minor. The total industry VOC emissions from processes based on cumene peroxidation were estimated in this study to be 4030 Mg in 1980, with most of the uncontrolled VOC emissions coming from fugitive sources.

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[1] "No Switch from Cumene, Say Phenol Manufacturers," Chemical Engineering 86(8), 64 (Apr. 9, 1979).

[2] S. A. Cogswell, "Phenol," pp 686.5021A—686.5023J in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (October 1978).

[3] S. A. Cogswell, "Acetone," p 604.5032A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1978).

[4] "Chemical Profile in Phenol," p. 9 in Chemical Marketing Reporter, Feb. 6, 1978.

[5] S. A. Cogswell, "Acetone," pp 604.5031 C—D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1978).

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Table VII-1. Emission Summary for the Model Plant Using Allied Technology

Emission Source	Vent Designation (Fig. III-1)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
Cumene oxidation	A	471.0	11.9
CHP concentration	B	41.7	0.83
Crude-acetone (light-ends) column	C	6.8	0.002
Acetone finishing column	D	14.8	0.59
Other distillation column	E	1.4	1.4
Storage and handling vents	H, I	20.8	5.1
Fugitive	J	37.8	10.9
Secondary			
Wastewater treatment	K	0.41	0.41
Incineration of tars	L	0.13	0.13
Total		594.8	31.3

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Table VII-2. Emission Summary for the Model Plant Using Hercules Technology

Emission Source	Vent Designation (Fig. III-2)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
Cumene oxidation	A	52.8	11.9
Oxidate wash/separation	B	1.8	0.25
CHP concentration	C	27.8	0.56
CHP cleavage	D	10.8	0.43
Light-ends column	E	6.8	0.003
Acetone finishing column	F	14.8	0.59
Other distillation column	G	1.4	1.4
Storage and handling vents	H, I	20.8	5.0
Fugitive	J	37.8	10.9
Secondary			
Wastewater treatment	K	0.62	0.62
Incineration of tars	L	0.17	0.17
Total		175.6	31.8

APPENDIX A

Table A-1. Properties of Acetone*

Synonyms	2-Propanone, dimethyl ketone, B-ketone propane, methyl ketone, pyroacetic ether
Molecular formula	C_3H_6O
Molecular weight	58.08
Physical state	Liquid
Vapor pressure	400 mm at 39.5°C
Vapor specific gravity	2.0
Boiling point	56.2°C at 760 mm
Melting point	-95.35°C
Density	0.7972 g/ml at 15°C/4°C
Water solubility	Infinite

*From: J. Dorigan *et al.*, "Acetone," p. AI-20 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals A-C)*, MTR - 7248, Rev. 1, Appendix I, Mitre Corp., McLean, VA (September 1976).

Table A-2. Properties of Cumene*

Synonyms	Isopropyl benzene, 2-phenyl propane, cumol
Molecular formula	C_9H_{11}
Molecular weight	120.21
Physical state	Liquid
Vapor pressure	6.56 at 25°C
Vapor specific gravity	4.1
Boiling point	152°C
Melting point	-96°C
Density	0.864 g/ml at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan et al., "Cumene," p. AI-306 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals A-C), MTR - 7248, Rev. 1, Appendix I, Metre Corp., McLean, VA (September 1976).

APPENDIX B

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

---

*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX C

EXISTING PLANT CONSIDERATIONS

Data reported on control devices and techniques used in existing Allied, Georgia Pacific, Monsanto, and Shell phenol/acetone plants are summarized in Table C-1 and discussed below.

1. Cumene Oxidation Vent

Allied reported[1] the use of a carbon adsorption system with an overall hydrocarbon removal efficiency of 92%. The carbon adsorber follows a refrigerated condenser. Georgia Pacific and Shell also reported[2,3] the use of carbon adsorption following a refrigerated condenser. Georgia Pacific reported[2] a control efficiency of 99% for their carbon adsorption unit including condensation, and Shell reported[3] design data from which a control efficiency of 83.4% was calculated for the carbon adsorption step. Monsanto reported[4,5] that they use a refrigerated condenser as the control device with a 90% control efficiency at 4 to 5°C and 85 psia.

2. Oxidate Wash/Separation Vent

The oxidate wash/separation vent is not applicable to plants using the process based on Allied technology. Georgia Pacific and Monsanto, who use Hercules technology, reported[2,4] emission control by condensation. Georgia Pacific reported[2] a control efficiency of 84%.

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[1] C. W. Stuewe, IT Enviroscience, Trip Report for Visit to Allied Chemical Corp., Philadelphis, PA, Mar. 16, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

[2] C. W. Stuewe, IT Enviroscience, Trip Report for Visit to Georgia Pacific Corporation, Plaquemine, LA, Aug. 2, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

[3] Shell Oil Co./Shell Chemical Co., Deer Park, TX, Texas Air Control Board Permit Application for phenol-2 as revised May 9, 1975.

[4] C. W. Stuewe, IT Enviroscience, Trip Report for Visit to Monsanto Chemical Intermediates Co., Alvin, TX, July 28, 1977 (on file at EPA, ESED, Research Triangle Park, NC)

[5] Texas Air Control Board, Permits 1985 and 1986 issued to Monsanto Co., Chocolate Bayou Plant, Alvin, TX, for phenol/acetone manufacture.

Table C-1. Control Devices and Techniques Reported by Existing Plants

Emission Source	Control Device or Technique Used by			
	Allied[a]	Georgia-Pacific[b]	Monsanto[c]	Shell[d]
Cumene oxidation	Carbon adsorption	Carbon adsorption	Pressurized refrigerated condensation	Carbon adsorption
Oxidate wash/separation	Not applicable	Condensation	Condensation	
CHP concentration	Chilled-brine condenser	Condensation	Condensation	
CHP cleavage and neutralization	No vent	Condensation on cleavage and vent water scrubber on neutralization	Vent condenser for cleavage and for neutralization	Water scrubber for cleavage
Light-ends column	Condensation	Incineration-existing boiler	Water scrubber	Incineration in existing fire box
Acetone finishing column	Water scrubber	Condensation	Condensation	Water scrubber
Other distillation columns	Water scrubber for cumene recovery distillation; condensation on AMS, phenol, and acetophenone columns	Incineration in existing boiler on AMS and heavy-ends columns	Condensation on crude acetone/phenol, heavy-ends, and phenol purification columns	Incineration in existing fire box for crude acetone columns
Storage	IFR[e] on 2 acetone and 2 cumene tanks; vent scrubber on other acetone tanks	Water scrubber on acetone day tanks and cleavage product tank; vent condensers on acetone storage and light- and heavy-oil tanks	IFR for crude AMS and most acetone tanks	FR[f] on acetone tanks; vent scrubber on phenol, heavy-ends, and light HC tanks; refrigerated condensation on cumene/CHP and on crude-product tanks
Handling	Vent scrubber on acetone loading	Control on acetone by unnamed device		Vent scrubber on acetone loading

[a] See ref 1. [b] See ref 2. [c] See ref 4. [d] See ref 3. [e] Internal floating-roof tank. [f] Floating-roof tank.

3. CHP Concentration Vent

The CHP concentration column is operated under vacuum. Allied reported[1] using chilled-brine condensation to control the vent. Georgia Pacific reported[2] a control efficiency of 95% using condensation. Monsanto also reported[4] using condensation to control the vent.

4. CHP Cleavage and Neutralization Vents

Georgia Pacific reported[2] a cleavage ejector condenser for the cleavage vent with a control efficiency of 93% and a water scrubber on the neutralization vent. Condensation on both the cleavage and the neutralization vents was reported by Monsanto.[4] Shell reported[3] use of refrigerated condensation followed by water scrubbing of the cleavage reactor vent. Based on the data supplied a control efficiency of 96% was calculated for the Shell scrubber.

5. Light-Ends Column Vent

Allied reported[1] the use of condensation to control the light-ends column vent. Georgia Pacific and Shell reported[2,3] that they incinerated the vent stream by using it as part of the fuel for existing fire boxes. Control by aqueous scrubbing of the vent and eventual disposal of the wastewater by underground injection was reported[4] by Monsanto.

6. Acetone Finishing Column Vent

Georgia Pacific and Monsanto reported[2,4] the use of condensation for control of the acetone finishing column vent. Allied and Shell use aqueous scrubbing for control of this vent.[1,3] The Shell scrubber follows refrigerated condensation, and based on the data reported,[3] a control efficiency of 95% was calculated for the water scrubber.

7. Other Distillation Column Vents

Allied, Georgia Pacific, Shell, and Monsanto reported[1—4] varying control techniques for selected distillation column vents. The control techniques reported were aqueous scrubbing, condensation, and incineration.

8. Storage

Allied, Shell, and Monsanto reported[1,3,4] the use of floating-roof tanks for storage of acetone. Floating-roof tanks were also reported by Allied[1] for cumene storage and by Monsanto[4] for crude-AMS storage. Aqueous scrubbing of acetone tank vents was reported[1—3] by Allied, Georgia Pacific, and Shell. The use of condensation on selected tanks was reported[2,3] by Georgia Pacific and Shell. Shell also reported[3] using aqueous scrubbing, of tank vents containing phenol, for hydrocarbon and odor control.

9. Handling

Allied and Shell reported[1,3] using aqueous scrubbing to control acetone-loading vents. Georgia Pacific reported[2] a control efficiency of 70% on the acetone-loading vents.

APPENDIX D

COST ESTIMATE PROCEDURE FOR PROCESS EMISSION CONTROL WITH CARBON ADSORPTION

A. EMISSION TO CARBON ADSORPTION

From cumene oxidation vent of a model plant using Allied technology:

$$\text{Cumene}\quad \frac{377\ \text{kg}}{\text{hr}} \times \frac{2.2\ \text{lb}}{\text{kg}} \times \frac{\text{hr}}{60\ \text{min}} \times \frac{\text{lb-mole}}{120.2} \times \frac{359\ \text{ft}^3}{16\ \text{moles}} = 41\ \text{scfm}$$

$$\text{Other VOC}\quad \frac{94\ \text{kg}}{\text{hr}}\ \text{at}\ 58.1\ \text{lb/lb-mole} = \underline{21}\ \text{scfm}$$

$$\text{Total VOC}\qquad 62$$

$$\text{Spent air}\ 40580\ \text{kg/hr at}\ 28.5\ \text{lb/lb-mole} = \underline{18{,}740}\ \text{scfm}$$

$$\text{Total waste gas to carbon adsorption} = 18{,}800\ \text{scfm}$$

$$\text{Cumene}\quad \frac{377\ \text{kg}}{\text{hr}} \times \frac{2.2\ \text{lb}}{\text{kg}} \times \frac{\text{hr}}{60\ \text{min}} = 13.8\ \text{lb/min}$$

$$\text{Other VOC}\quad \frac{94\ \text{kg}}{\text{hr}} = \underline{3.5}\ \text{lb/min}$$

$$\text{Total VOC}\qquad 17.3\ \text{lb/min}$$

$$\text{VOC content}\quad \frac{17.3\ \text{lb/min}}{18.8 \times 1000\ \text{scf/min}} = 0.92\ \text{lb of VOC/1000 scf}$$

B. TOTAL INSTALLED CAPITAL

From Fig. IV-1 of the control device evaluation report for carbon adsorption,[1] the December 1979 installed capital cost of a carbon adsorption system for 18,800 scfm of waste gas is $574,000

C. CARBON REQUIREMENT

For a VOC content of 0.92 lb/1000 scf and an estimated loading capacity of 11 lb of VOC/100 lb of carbon the carbon requirement shown in Fig. II-1 of the carbon adsorption report[1] is 8 lb of carbon/1000 scf.

---

[1] H. S. Basdekis and C. S. Parmele, IT Enviroscience, Control Device Evaluation. Carbon Adsorption (January 1981) (EPA/ESED report, Research Triangle Park, NC).

D. NET ANNUAL COST

From Fig. IV-2 of the carbon adsorption report[1] the annual cost of a carbon adsorption system for 18,800 scfm with 8 lb of carbon/1000 scf and regenerated at a rate of 0.3 lb of steam/lb of carbon is $13.8/scfm if no credit is taken for recovered VOC, or $259,000.

From Table VI-1 of this report the VOC adsorbed is

$$\frac{4021\ \text{Mg}}{\text{yr}} \times \frac{2205\ \text{lb}}{\text{Mg}} = 8{,}866{,}000\ \text{lb/yr}.$$

Using an estimated recovery of 90% of the VOC adsorbed and a raw-material value of $0.181/lb of VOC the recovery credit is as follows:

$$\frac{8{,}866{,}000\ \text{lb}}{\text{yr}} \times 0.9 \times \frac{\$0.181}{16} = \$1{,}443{,}000/\text{yr}.$$

The net annual cost is

$$\$259{,}000 - \$1{,}443{,}000 = -\$1{,}184{,}000, \text{ or a savings.}$$

The cost effectiveness is

$$\frac{-\$1{,}184{,}000/\text{yr}}{4021\ \text{Mg/yr}} = -\$294/\text{Mg removed.}$$

REPORT 7

LINEAR ALKYLBENZENE

C. A. Peterson, Jr.

IT Enviroscience
9041 Executive Park Drive
Knoxville, Tennessee 37923

Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

February 1981

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Linear alkylbenzene (LAB) production was selected for consideration because preliminary estimates indicated that emissions of volatile organic compounds (VOC) are relatively high and that the predominant manufacturing process emits significant quantities of benzene, which was listed as a hazardous pollutant by the EPA in the Federal Register on June 8, 1977. This report has been changed to an abbreviated format because the data received during its preparation indicate that benzene emissions from a new LAB plant can be satisfactorily controlled and because of the low vapor pressures of all the other VOC used in LAB manufacture. LAB is a viscous liquid with low vapor pressure at ambient conditions. It is normally processed at elevated temperatures, where the viscosity is lower and the vapor pressure is higher. Benzene, the predominant emission, is a volatile liquid at ambient conditions but is emitted as a gas. (See Appendix A for pertinent physical properties.)

B. USAGE AND GROWTH

Table II-1 (refs. 1—3) shows LAB usage and growth rate. The predominant end use for LAB is in the manufacture of linear alkyl sulfonate for use in synthetic detergent formulations.

The domestic LAB nameplate production capacity for 1979 was reported to be 304,000 Mg, with 93% of this capacity being utilized.[1,2] Actual production plant capacities vary with product mix and operating conditions. With the planned new LAB capacity announced by Conoco for 1982 there should be sufficient capacity to supply domestic demand through 1994 if it grows 2% annually as projected.

C. DOMESTIC PRODUCERS[1,2]

As of 1980 there were four domestic producers of LAB. Table II-2 (refs. 1,2) lists the producers, the plant locations, and the processes being used; the plant locations are shown in Fig. II-1. Approximately 36% of the 304,000-Mg/yr domestic capacity is based on the olefin conversion process wherein n-paraffin feedstock is dehydrogenated to mono-olefins before alkylation with benzene to LAB. The rest of the domestic capacity uses the chlorination process, wherein the n-paraffin feedstock is chlorinated to mono-chloroparaffin before alkylation

Table II-1. Linear Alkylbenzene (LAB) Usage and Growth[a]

Year	Production (Gg/yr)	Growth (%/yr)
1966	218	
1967	218	
1968	253[b]	3.3
1969	240	-5.2
1970	251	4.5
1971	249[c]	-0.5
1972	238[c]	-4.7
1973	226[d]	-5.0
1974	242	7.0
1975	224[e]	-7.1
1976	245	9.1
1977	239[d]	-2.4
1978	239[d]	
1979	284	18.8

[a] See refs 1-3.

[b] Temporary production spurt caused by a fire in the Shell Nederland Chemie NV wax cracking plant at Pernis, The Netherland.

[c] Export shipments to Europe dropped when new Spanish LAB plant became operational.

[d] Tight supplies of raw materials, both chlorine and benzene in 1973 and *n*-paraffin in 1977 and 1978, limited production.

[e] Recession.

Table II-2. Linear Alkylbenzene (LAB) Capacity[a]

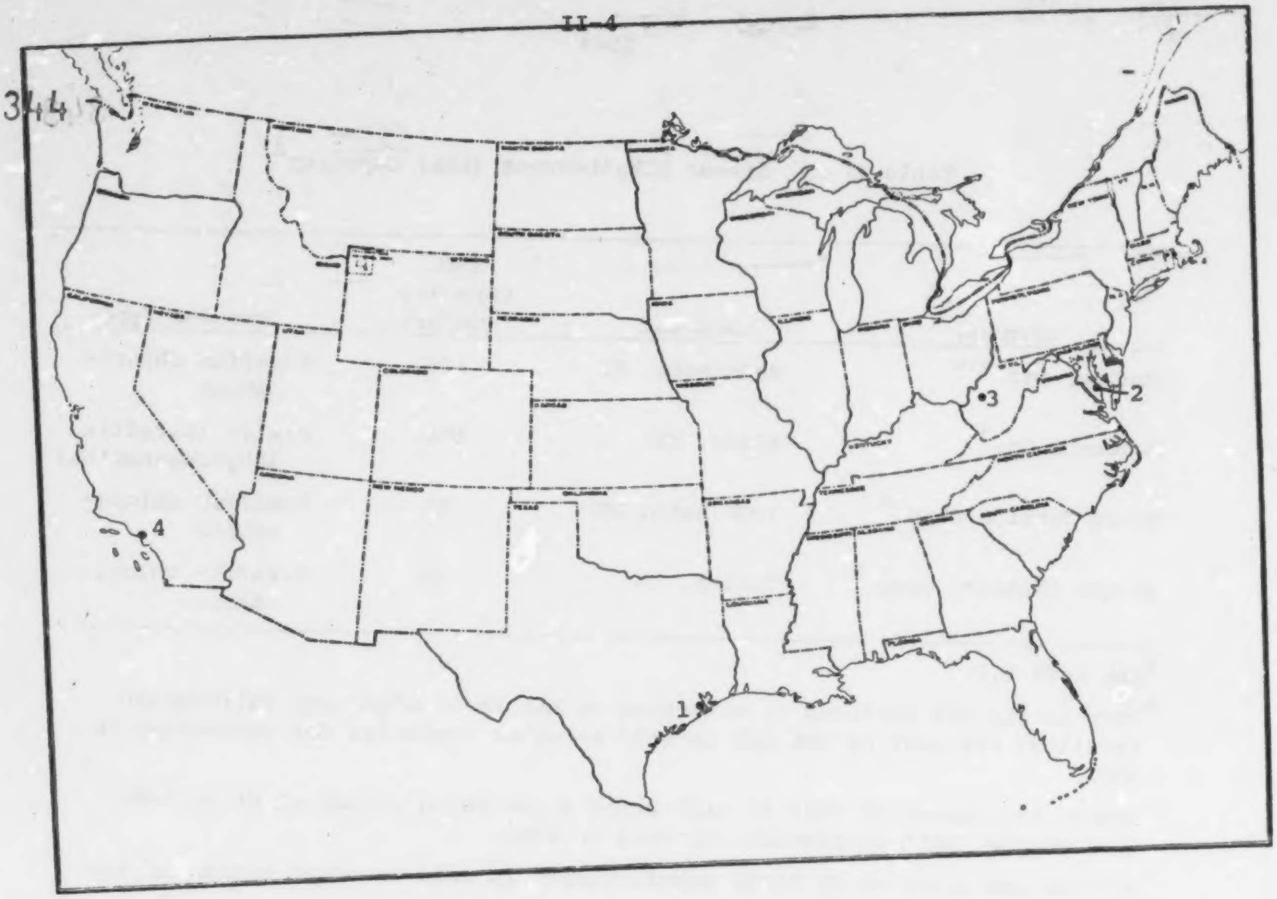
Company	Location	1980 Capacity (Gg/yr)	Process Type
Conoco, Inc.[b,c]	Baltimore, MD	109	Paraffin chlorination
Monsanto Co.[d]	Alvin, TX	109	Olefin (paraffin dehydrogenation)
Union Carbide Corp.[d]	Institute, WV	66	Paraffin chlorination
Whitco Chemical Corp.[b]	Carson, CA	20	Paraffin chlorination

[a] See refs 1,2.

[b] Part of the LAB produced is converted to LAS in an adjoining sulfonation facility; the rest of the LAB is sold to other companies for conversion to LAS.

[c] Conoco has announced that it will build a new 68-Gg/yr LAB plant at Lake Charles, LA, with completion expected in 1982.

[d] All the LAB produced by these manufacturers is sold to other companies for conversion to LAS.



(1) Monsanto Co., Alvin, TX
(2) Conoco Chemicals Div., Baltimore, MD
(3) Union Carbide Corp., Institute, WV
(4) Witco Chemical Corp., Carson, CA

Fig. II-1. Locations of Plants Manufacturing LAB

with benzene to LAB. Data are not availabale on the comparative economics of these two production routes for the manufacture of LAB.

Prior to 1966 the principal alkylate used for manufacture of synthetic detergents was a branched-chain material produced by the alkylation of propylene tetramer with benzene. Sulfonation of this alkylate produced a cheap and effective alkylbenzene sulfonate (ABS) detergent used in most of the synthetic detergent formulation. Since ABS is resistent to biodegradation, governmental regulations forced the detergent industry to switch to LAB as the alkylate material for sulfonation to detergent alkylate. Linear alkylate sulfonate (LAS) produced from LAB is much more biodegradable in natural water systems than the branched-chain alkylate sulfonate (ABS) it replaced.

The manufacture of LAS-based synthetic detergents based on the use of LAB is a mature industry with small growth potential. Newer detergents are coming on the market. These new synthetic detergents are based on linear paraffin sulfonates and the nonionic, ethoxylated mixed linear alcohols. LAB is expected to continue its dominant role in synthetic-detergent manufacture, but the newer detergent materials are taking over the growth portion of the detergent market.

D. REFERENCES*

1. R. F. Modler *et al.*, "Normal Paraffins (C_9-C_{17})," pp. 683.5022D—683.5022H in *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA (September 1980).

2. R. F. Bradley, "Linear and Branched Alkylbenzenes," pp. 610.5000A—610.5000R in *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA (January 1979).

3. "Manual of Current Indicators--Supplemental Data," p. 240 in *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA (October 1980).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Two major processes are used to manufacture linear alkylbenzene (LAB) in the United States. Approximately 64% is manufactured by three companies using the paraffin chlorination process, and approximately 36% is manufactured by one company using the olefin (paraffin dehydrogenation) process (see Table II-2). The projected growth rate for the domestic total LAB market is only 2% per year.[1]

The only significant foreign process not normally used in the United States uses as feedstock the linear alpha olefins produced by Shell's wax cracking process (Shell Nederland Chemie NV, Pernis, The Netherlands). These linear alpha olefins are alkylated with benzene at several locations to produce a linear alkylbenzene (LAB), but the LAB from linear alpha olefins produces a detergent with a slightly different balance of detergent properties. When n-paraffins were in short supply during the late 1970s, linear alpha olefins were used as raw material for LAB in the United States.[1,2]

B. OLEFIN PROCESS

1. Basic Reactions and Process Description[1--5]

LAB is produced from n-paraffins (C_{10} to C_{14} mixtures) and benzene in a two-step sequence of reactions. In the first step n-paraffins are dehydrogenated to n-olefins by passing hot, vaporized paraffins through a catalyst bed, where hydrogen is split off from the paraffin molecule, leaving an olefinic double bond.[1,3] A simple illustration of this reaction is

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 \longrightarrow R_1CH{=}CH\text{-}R_2 + H_2$$

[R_1 and R_2 represent groups of various chain lengths, from a minimum of hydrogen to C_nH_{2n+1} (alkyl).]

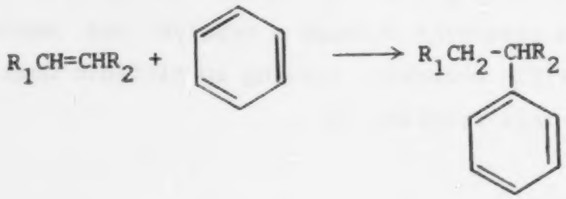
The resultant olefin mixture contains some alpha olefins (10 to 30%), as well as a mixture of internal olefins, unreacted paraffins, some diolefins, and lower molecular weight "cracked" materials. Space velocities are high and residence times are low through the catalyst bed to minimize the amount of isomerization, polymerization, coking, and chain scission that can occur. The exit gas mixture is quenched by contact with a cold liquid stream to minimize thermally promoted side reactions after the vapor exits from the catalyst bed.

Reaction conditions are selected to achieve an economic balance between the amount of unreacted paraffin left in the olefin mixture and the amount of material degraded to low-molecular-weight oils and residual coke.

Gas separated from the reaction product consists of hydrogen and low-molecular-weight hydrocarbons such as methane, ethane, ethylene, propane, etc. This gas can be used as fuel in the process burners, can be piped to an auxiliary process that uses hydrogen, or can be vented to a flare stack. The most common practice is to use the mixed gas stream as a process fuel.

The process flow diagram shown in Fig. III-1 was developed from literature sources to illustrate the olefin process. Some variations from the flowsheet in Fig. III-1 exist in current industrial practice, but it is accurate enough to be useful for air emission evaluations.

In the second reaction step benzene is reacted with the olefin stream from the first reaction step in the presence of an alkylation catalyst to form the linear alkylbenzene. A simple illustration of this reaction is



The benzene is dried by azeotropic distillation to remove all traces of water before the above reaction occurs. In the alkylation reactor the benzene, olefin, and alkylation catalyst are blended intimately and held at reaction conditions long enough for the alkylation reaction to go to completion. Hydrogen fluoride is the catalyst of choice for alkylation of benzene with linear olefins, since

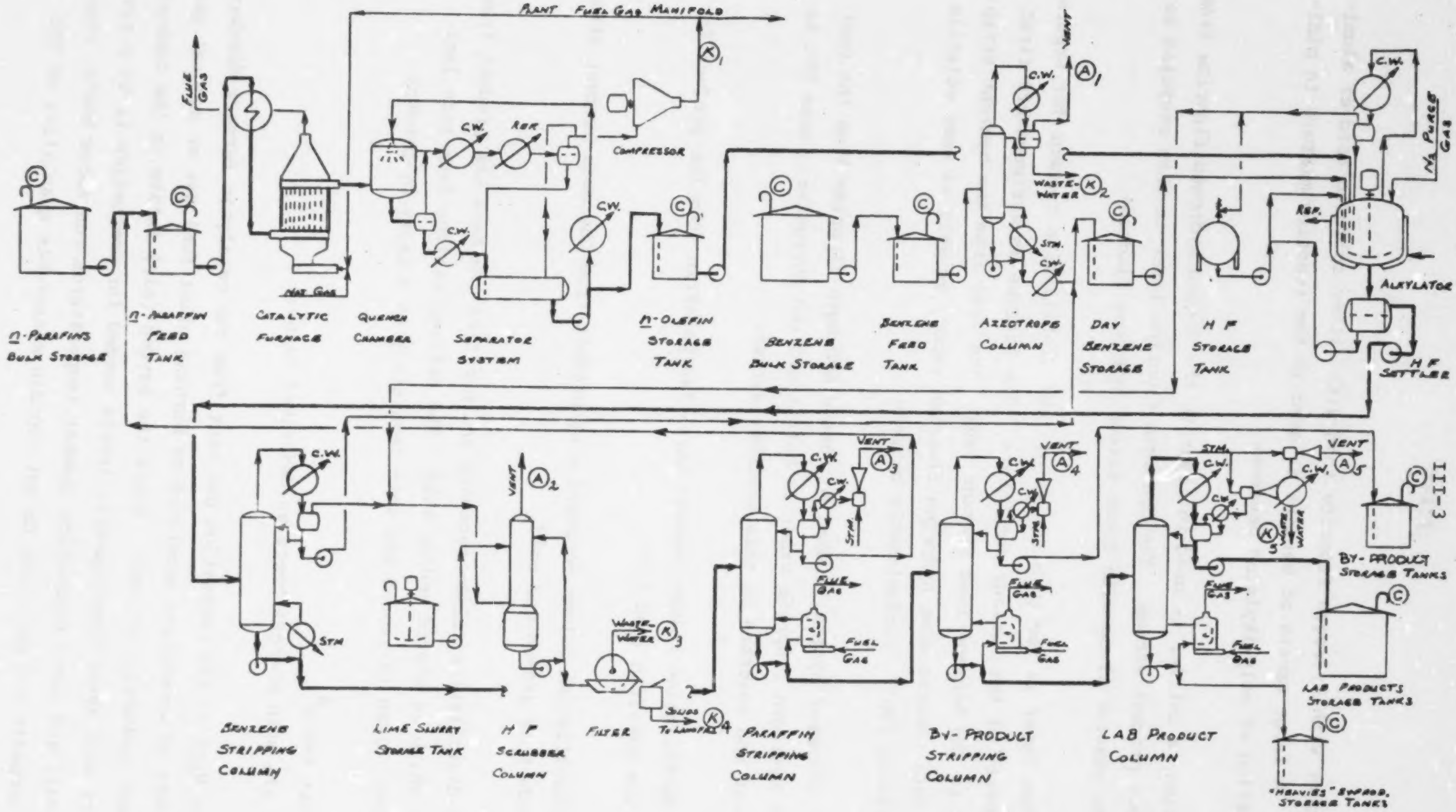

PLANT FUEL GAS MANIFOLD
FLUE GAS
K1
COMPRESSOR
C.W.
REF.
C
NAT GAS
VENT
A1
WASTE-WATER
K2
STM.
N2 PURGE GAS
ALKYLATOR
n-PARAFFINS BULK STORAGE
n-PARAFFIN FEED TANK
CATALYTIC FURNACE
QUENCH CHAMBER
SEPARATOR SYSTEM
n-OLEFIN STORAGE TANK
BENZENE BULK STORAGE
BENZENE FEED TANK
AZEOTROPE COLUMN
DAY BENZENE STORAGE
H F STORAGE TANK
H F SETTLER
A2
A3
A4
A5
K3
K4
K5
WATER
FUEL GAS
FLUE GAS
SLUDGE TO LANDFILL
BENZENE STRIPPING COLUMN
LIME SLURRY STORAGE TANK
H F SCRUBBER COLUMN
FILTER
PARAFFIN STRIPPING COLUMN
BY-PRODUCT STRIPPING COLUMN
LAB PRODUCT COLUMN
BY-PRODUCT STORAGE TANKS
LAB PRODUCTS STORAGE TANKS
"HEAVIES" BYPROD. STORAGE TANKS

Fig. III-1. Flow Diagram for LAB Olefin Process Model Plant with Uncontrolled Emissions

yields are higher with hydrogen fluoride than with either sulfuric acid or aluminum chloride. A large excess of benzene is used in the reaction mixture to minimize the formation of polyalkylated benzenes.

After alkylation, a settler is used to separate the liquid hydrogen fluoride from the hydrocarbon product stream. The hydrogen fluoride layer is then recycled to the alkylation reactor along with fresh makeup hydrogen fluoride.

The hydrocarbon layer is fed to a series of four distillation columns for separation and recovery of the various components. The benzene is stripped off first and returned to the benzene feed storage tank. The vent from the benzene stripping column does contain some hydrogen fluoride vapor, as well as some volatile organic chemicals (VOC), predominantly benzene.

A lime-water scrubber system is used to remove hydrogen fluoride from the vent gases, since hydrogen fluoride vapor is both toxic and corrosive. Some VOC is also condensed and absorbed in this scrubber system.

The second distillation column removes unreacted paraffin from the product for recycle to the paraffin feed tank.

The third distillation column recovers a by-product from the main product stream. This by-product is stored and sold.

The fourth distillation column recovers and purifies the main LAB product from the plant, which is stored and/or sold. The bottoms residue from this last distillation column is stored and sold separately as a heavy by-product.

2. Main Process Vents[3]

There are six main process vents as described below:

a. Combustion Vent -- The combustion gas vent from the catalytic furnace discharges the products of combustion generated by burning plant fuel gas or natural gas in the furnace combustion chamber. Since the oxygen (air) intake to the combustion chamber is well above stochiometric levels needed for combustion (2 to 3 times theoretical) and since combustion chamber temperatures run above 900°C, combustion is complete and emissions do not contain measurable quantities of VOC.

b. Benzene Azeotrope Column Vent A_1 -- The vent after the condenser on the benzene azeotrope column does contain significant levels of benzene vapor. The amount of benzene emitted here is influenced by the amount of noncondensables (inert gases and air) venting from the column and by the operating temperature and design of the reflux condenser.

c. Hydrogen Fluoride Scrubber Vent A_2 -- This vent is the discharge vent from the hydrogen fluoride scrubber. The amount of VOC emitted here is influenced by the inert gases and air venting from this scrubber system, along with the operating temperature of the scrubber fluid, the solubility of the VOC in the scrubber fluid, and the purge rate of the scrubber fluid. The vent gases from the hydrogen fluoride scrubber go to a flare, which acts as an emission control device.

Paraffin stripping column vent A_3 -- The paraffin stripping column operates under a vacuum of 24 kPa absolute, and the column is vented through a steam jet to the atmosphere. Any VOC that exit from the vacuum line after the vent condenser would be discharged to the atmosphere. Air or inert gases that enter the column and exit through the vacuum line would sweep VOC with the noncondensables. Operating temperature and design of the vent condenser influence the amount of VOC emitted. The reboiler furnace on the column emits direct combustion products to the atmosphere. Fuel for this furnace is plant fuel gas or natural gas.

Lights stripping column vent A_4 -- The lights stripping column operates under a vacuum of 13.3 kPa absolute, and the column is vented through a steam jet to the atmosphere. Any VOC that exit from the vacuum line after the vent condenser would be discharged to the atmosphere. Air or inert gases that enter the column and exit through the vacuum line would sweep VOC with the noncondensables. Operating temperature and design of the vent condenser influence the amount of VOC emitted. The reboiler furnace on the column emits combustion products from the direct combustion of plant fuel gas or natural gas.

LAB product column vent A_5 -- This vent operates under a vacuum of 1.3 kPa absolute, with a two-stage steam jet with intercondenser used as the vacuum source. The discharge from the primary jet is condensed and discharged as wastewater, and the secondary jet discharges to the atmosphere. Any VOC that exit from the vacuum line after the vent condenser would be condensed with the jet condensate or be vented to the atmosphere. (It is estimated that almost all the VOC in the vacuum line would be condensed and discharged as a wastewater contaminant, probably as an oily film on the water.) Air or inert gases that enter the column and exit through the vacuum line would sweep VOC with the noncondensables. Operating temperature and design of the vent condenser influence the amount of VOC emitted. The reboiler furnace on the column emits combustion products directly to the atmosphere. Fuel for this furnace is plant fuel gas or natural gas.

3. Other Emission Sources

Fugitive leaks throughout the process can emit benzene, paraffin, olefin, LAB, by-products, or hydrogen fluoride. Corrosion can occur in the alkylation section wherever moisture from air or water lines contact streams containing hydrogen fluoride. Benzene distillation columns operate above atmospheric pressure. Pressure in the process side of the reflux condenser may be higher than the pressure in the cooling-water side of the reflux condenser. Any leaks in heat exchangers where the pressure of the organic side is higher than the pressure on the water side would permit the cooling water to be contaminated with VOC. This VOC would eventually be released into the atmosphere from the cooling tower system.

Storage and handling emission sources (labeled C on Fig. III-1) include benzene, paraffin, olefin, LAB, and by-products.[3]

There are five potential sources of secondary emission (labeled K on Fig. III-1): the hydrogen-hydrocarbon gas from the compressor on the dehydrogenation (paraffin to olefin) system, the wastewater from the benzene azeotrope column receiver, the wastewater from the hydrogen fluoride scrubber system filter, the wet solids from the hydrogen fluoride scrubber system filter, and the wastewater from the LAB column jet condenser. The hydrogen-hydrocarbon gas from the dehydrogenation system is a satisfactory fuel in the direct-fired furnaces of the catalytic furnace and the direct-fired reboilers of the three columns, replacing natural gas as fuel for these units. Since this process gas burns cleanly and completely, no VOC is emitted when the gas is used as fuel. The wastewater from the benzene azeotrope column receiver is saturated with benzene. The amount of wastewater from the azeotrope column receiver is fixed by the amount of water in the benzene raw material purchased for use in this plant. The wastewater from the hydrogen fluoride scrubber system filter normally contains a mixture of VOC, predominantly benzene with some paraffin, olefin, LAB, etc. The solids from the HF scrubber system filter are discharged at the rate of about 9000 g/Mg of product (dry basis). Washing the filter cake with fresh water will transfer most of the VOC to the wastewater stream.[3] The wastewater from the LAB jet condenser contains very low levels of VOC. This wastewater stream is added to the other plant wastewater streams.

4. Process Variations

There are many possible variations of the paraffin dehydrogenation step. (Existing plant considerations are given in Appendix B.) Various catalysts can be used to accelerate dehydrogenation, and one version (thermal) can dehydrogenate paraffins without a catalyst. Reaction times and temperatures vary, depending on the catalyst used. The reaction technique and type of catalyst can also change the amount of paraffin to olefin conversion and the amount of side reactions that occur. If a large amount of low-molecular-weight by-products is formed, these impurities may have to be stripped before the output stream is sent to alkylation.[3--5]

Alkylation can be catalyzed by various catalyst systems, such as hydrogen fluoride, sulfuric acid, and aluminum chloride. Reaction conditions and process vessel design can also influence the rate of alkylation and the amount of side reactions. For olefin alkylation with benzene, hydrogen fluoride is the catalyst of choice, since yields are higher and side reactions are lower than with other catalysts.[2] Excess benzene (usually 3 to 5 times theoretical quantity) is used to minimize the formation of polyalkylbenzene.[2,4]

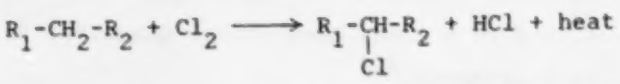
Alkylation catalyst selection, in turn, dictates the type of system used for catalyst removal. Hydrogen fluoride can be separated from the product stream by settling and decantation; hydrogen fluoride is too expensive to be discarded, recovery and recycling are necessary. The hydrocarbon layer is saturated with dissolved hydrogen fluoride, which must be removed by a distillation operation.[2--4]

Product cleanup is necessary after the alkylation step. Multiple distillation will separate the various hydrocarbon fractions. Benzene is normally removed first in a benzene stripping column. Residual hydrogen fluoride vapors are emitted during the benzene distillation, and will sweep some benzene vapor with them as they exit from the benzene stripping system. A hydrogen fluoride scrubber system must be used to remove hydrogen fluoride vapors from the vent stream, since hydrogen fluoride is too toxic and corrosive to be vented to the atmosphere.[2] After benzene is removed, vacuum stripping distillation is used to remove residual paraffin for recycle. A second vacuum distillation at lower absolute pressure is used to remove a by-product fraction. A third distillation at even lower absolute pressure is used to separate the main LAB product stream from a "heavies" by-product fraction. Various distillation schemes and various designs of distillation towers can be used to accomplish this separation of the alkylate hydrocarbon into various recycle, by-product, and product fractions. Some VOC will be emitted by the vent lines or vacuum systems used on each distillation column.

C. LAB CHLORINATION PROCESS

1. Basic Reactions and Process Description[1,6--8]

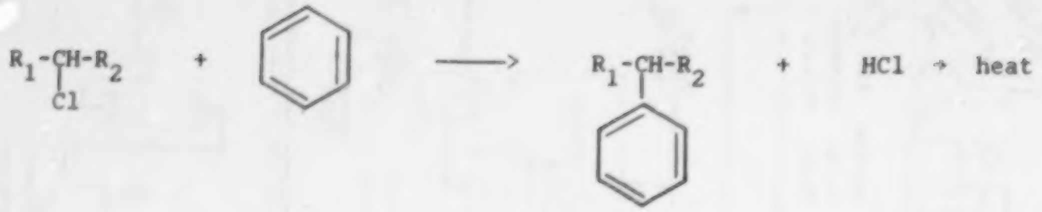
LAB is produced from n-paraffins (C_{10} to C_{14} mixtures) and benzene in a two-step sequence of reactions. In the first step, dry n-paraffins are reacted with gaseous chlorine to form n-chloroparaffins and by-product HCl. Ultraviolet light is used to promote the reaction. A simple illustration of this reaction is



$$R_1\text{-}CH_2\text{-}R_2 + Cl_2 \longrightarrow R_1\text{-}\underset{\substack{|\\ Cl}}{CH}\text{-}R_2 + HCl + \text{heat}$$

[R_1 and R_2 represent groups of various chain lengths, from a minimum of hydrogen to C_nH_{2n+1} (alkyl)]. An excess of n-paraffin is used in this reaction step to minimize the formation of chloroparaffin with more than one chlorine attached to a single paraffin chain. Reactants and equipment are kept "dry" to minimize the corrosive attack of wet hydrogen chloride on metallic equipment.

In the second reaction step dry benzene is reacted with the crude chloroparaffin mixture in the presence of aluminum chloride catalyst to form linear alkylbenzene (LAB). A simple illustration of this reaction is



An excess of benzene is used in this reaction step to minimize the formation of polyalkylbenzenes. In addition to by-product hydrogen chloride, other degradation products and by-products are formed. Some of these by-products and degradation products are olefins, short-chain paraffins, short-chain alkylbenzenes, polyalkylbenzenes, and miscellaneous "tars."

The process flow diagram shown in Fig. III-2 was developed from open literature sources to illustrate the paraffin chlorination process for the manufacture of linear alkylbenzene (LAB).

After alkylation the catalyst sludge is separated from the crude LAB by settling. The catalyst sludge is then hydrolyzed with water to separate the water-soluble aluminum chloride from the organic materials in the sludge. The organic materials recovered after hydrolysis are a complex mixture of benzene, LAB, and various degradation products or tars. Since the tars content is high, this stream of organic materials is collected and used for fuel or is sold.

The crude LAB is washed with alkaline water to neutralize it and is then separated from the alkaline wash by decanting. The crude LAB is washed again with water and is then separated from the water layer by another decanting operation. The water layers from the hydrolysis and washing steps are sent to the plant wastewater treatment facility.

After the washing step, the crude LAB is sent through a series of distillation columns to separate the crude LAB mixture into its various components.

The first distillation column operates at atmospheric pressure and strips residual benzene out of the crude LAB mixture. This recovered benzene is returned to the benzene feed tank.

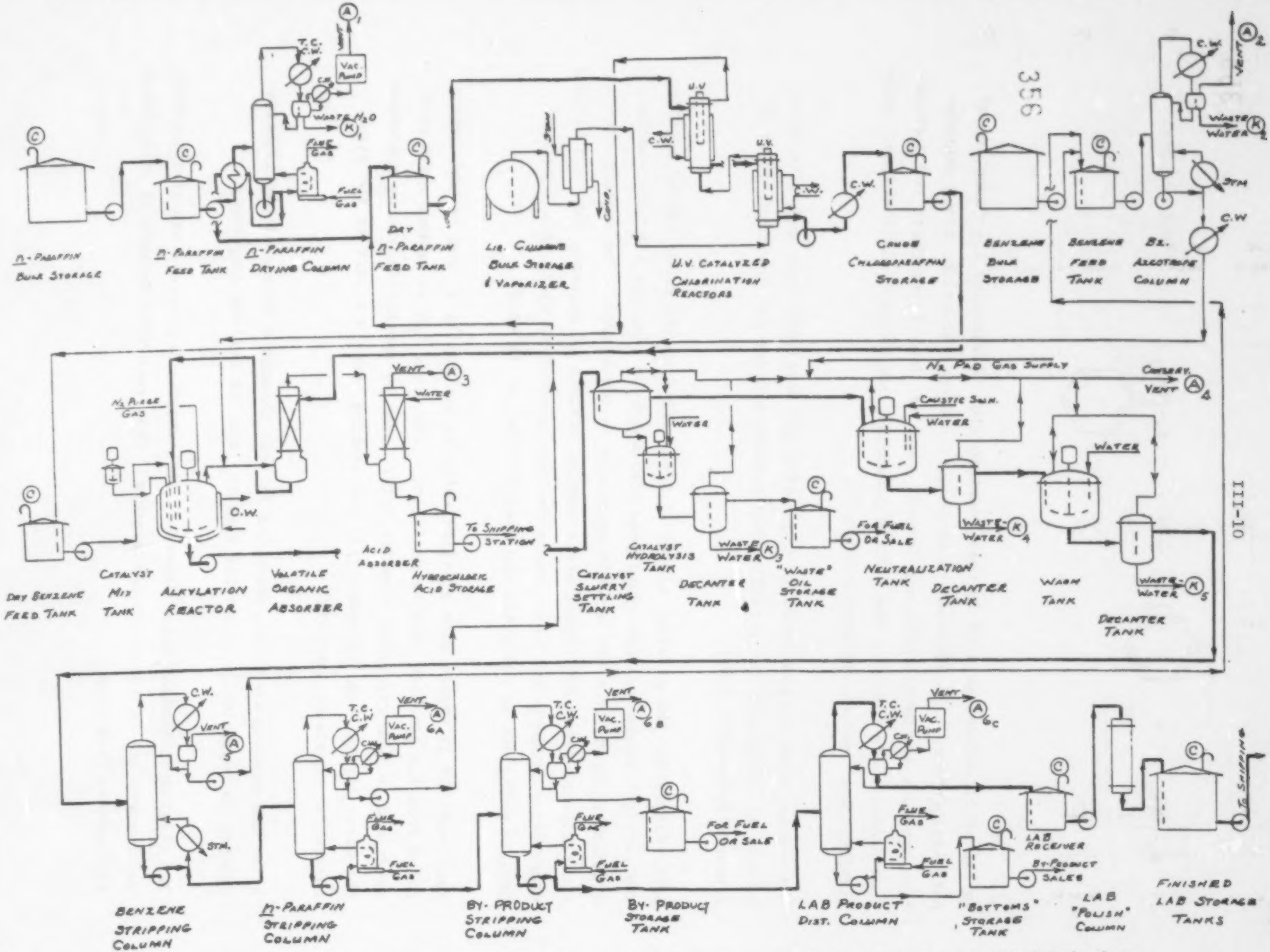

C
n-Paraffin Bulk Storage
n-Paraffin Feed Tank
n-Paraffin Drying Column
T.C. C.W.
C.W.
Vac. Pump
Vent
A1
Waste H2O
K1
Flue Gas
Fuel Gas
Dry n-Paraffin Feed Tank
Liq. Chlorine Bulk Storage & Vaporizer
Stm
Cond.
U.V.
C.W.
U.V. Catalyzed Chlorination Reactors
Crude Chloroparaffin Storage
Benzene Bulk Storage
Benzene Feed Tank
Bz. Azeotrope Column
Vent
A2
Waste Water
K2
Stm
N2 Purge Gas
O.W.
Dry Benzene Feed Tank
Catalyst Mix Tank
Alkylation Reactor
Volatile Organic Absorber
Vent
A3
Water
Acid Absorber
To Shipping Station
Hydrochloric Acid Storage
N2 Pad Gas Supply
Conserv. Vent
A4
Caustic Soln.
Water
Catalyst Slurry Settling Tank
Catalyst Hydrolysis Tank
Decanter Tank
Waste Water
K3
"Waste" Oil Storage Tank
For Fuel or Sale
Neutralization Tank
Decanter Tank
Waste-Water
K4
Wash Tank
Decanter Tank
Waste-Water
K5
Benzene Stripping Column
Vent
A5
Stm.
n-Paraffin Stripping Column
A 6A
By-Product Stripping Column
A 6B
By-Product Storage Tank
For Fuel or Sale
LAB Product Dist. Column
A 6C
"Bottoms" Storage Tank
By-Product Sales
LAB Receiver
LAB "Polish" Column
Finished LAB Storage Tanks
To Shipping

Fig. III-2. Flow Diagram for LAB Chlorination Process Model Plant with Uncontrolled Emissions

The second distillation column operates under vacuum and strips residual n-paraffin out of the crude LAB mixture. The recovered n-paraffin is returned to the n-paraffin feed tank.

The third distillation column operates under vacuum and strips "light oil" (a low-molecular-weight mixture of alkylbenzene and tars) out of the crude LAB mixture. This recovered light oil is either sold as a lubricating oil basestock or is burnt as fuel.

The fourth distillation column operates under vacuum and separates the LAB products from the bottoms or residual high-boiling materials. The overhead LAB product is stored for final treatment. The bottoms are collected and sold as detergent base stock for use in the manufacture of motor oil additives.

The overhead LAB product is passed through a treatment system for removal of residual impurities and colored materials. After this final treatment the finished LAB is shipped to detergent manufacturers for conversion to linear alkylbenzene sulfonate (LAS) and incorporation into finished detergent formulations.

2. Main Process Vents[6--8]

The main process vents from the chlorination process are as described below:

a. Paraffin Drying Column Vent -- This vent is normally interconnected with storage tank vents in a connected vent system so that direct discharge from the column to the atmosphere does not occur.

b. Benzene Azeotrope Column -- The quantity of benzene in this column vent will vary depending on the wetness of the benzene feed to the azeotrope column and on the design of the azeotrope column condenser.

c. HCl Absorber System -- The hydrogen chloride gas out of the VOC absorber system carries some VOC with it, and the acid absorber is normally operated to minimize the quantity of VOC dissolved in the aqueous hydrochloric acid. The quantity will vary, depending on the temperature of the fluid in the VOC absorber and the vapor pressure of the mixed absorber fluid. Some of the VOC could be absorbed in the aqueous hydrochloric acid and then be removed from the acid stream.

d. Post-Alkylation Treatment Vents -- These vents include vents from catalyst settling, catalyst hydrolysis, catalyst hydrolysis decanting, product neutralization, product neutralization decanting, product washing, and product washing decanting. The seven vents are tied together with one common vent line that is padded with nitrogen. A conservation vent on this nitrogen-padded common vent line does discharge some VOC to the atmosphere.

e. Benzene Stripping Column Vent -- This vent can contain significant amounts of benzene vapor. The amount of benzene vented here is influenced by the amount of noncondensables (inert gases) venting from the column, and by the operating temperature and design of the reflex condenser.

f. Vacuum Pump (or Steam Jet Vent) on Paraffin Stripping Column -- This vent discharges the vapors from the column to the atmosphere. The discharge amount is influenced by the air in-leakage into the column and by the design and operating temperature of the reflux condenser.

g. "Light Oil" Stripping Column Vacuum Pump (or Steam Jet Vent) -- The amount of VOC contained in this vent stream varies, depending on design and operating conditions.

h. LAB Product Column Vacuum Pump (or Steam Jet Vent) -- This vent discharges the vapors from the column to the atmosphere. The amount of VOC discharged is influenced by the air in-leakage into the column and by the design and operating temperature of the column reflux condenser.

3. Other Emission Sources

Fugitive leaks throughout the process can emit benzene, paraffin, chloroparaffin, LAB, by-products, chlorine, or hydrogen chloride. Corrosion can occur in the chlorination and alkylation sections wherever moisture from air or process streams contact a process stream containing chlorine or hydrogen chloride. In some production plants benzene distillation columns operate above atmospheric pressure. Pressure in the reflux condenser may be higher than the pressure in the water cooling the condenser. Leaks in heat exchangers where the pressure on the organic side is higher than the pressure on the water side would permit contamination of the cooling water with VOC. The VOC would eventually be released into the atmosphere from the cooling tower system.

Storage and handling emission sources (labeled C on Fig.III-2) include benzene, paraffin, chloroparaffin, LAB, and by-products.[6--8]

There are five potential sources of secondary emissions (labeled K on Fig. III-2): the VOC-contaminated wastewater discharged from the n-paraffin drying column, the VOC-contaminated wastewater discharged from the benzene azeotrope column, the VOC-contaminated wastewater discharged from the catalyst hydrolysis decanter tank, the VOC-contaminated wastewater discharged from the neutralization decanter tank, and the VOC-contaminated wastewater discharged from the wash decanter tank. If steam jets with aftercondensers were used as vacuum pumps on the four vacuum distillation columns, the condensate from these steam jets would be contaminated with VOC and would constitute additional sources of potential secondary emissions. These various sources of wastewater will all carry dissolved and suspended VOC. They can be combined and sent to a plant wastewater treatment facility, but some of the VOC will escape to the air in the treatment plants.

4. Process Variations

There are many possible minor variations of the LAB chlorination process. (See Appendix B for existing plant considerations.) Various reaction conditions, the concentration, the use of pure versus impure chlorine, the reactor design, the use of reaction accelerators (such as ultraviolet lamps), and the techniques used to absorb the heat of reaction all influence the performance of a facility for LAB via chlorination. Additional factors that affect plant performance is the technique used to remove VOC from the exit stream of hydrogen chloride gas and the technique used to convert the by-product hydrogen chloride to salable or useful forms or to otherwise dispose of this acid gas.

Production of LAB via chloroparaffin can be handled in several ways. Chloroparaffins can be refined or separated from unreacted n-paraffins before alkylation, or the crude reaction mixture can be alkylated before the refining steps are taken. Another possible reaction route involves the conversion of chloroparaffins to olefins in a separate reaction step before the olefins are alkylated with benzene. The olefins could be refined or purified before alkylation. The commercial practice normally is the one-step approach, in which crude chloroparaffins are alkylated with excess benzene in the presence of aluminum chloride complex as the alkylation catalyst. Refining and separation then take place after alkylation. The techniques used to remove the heat of reaction and those used to remove VOC from the by-product hydrogen chloride gas also affect process results. Again, the techniques used to convert the by-product hydrogen chloride to useful or salable forms or to otherwise dispose of this acid gas also influence plant performance.

Distillation techniques are used for separation of the various fractions in the crude alkylate product. The distillation columns can vary in design and operating technique, but high temperatures and low pressures are needed for effective separation into useful fractions, recycle materials, and by-products.[6--8]

As an alternate to the use of a treatment system, some manufacturers react the distilled (overhead) LAB with sulfuric acid and caustic solutions to remove the residual impurities and colored materials.[6--8]

D. REFERENCES*

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3. C. A. Peterson, IT Enviroscience, Trip Report for Visit to Monsanto Chemical Company, Inc., Alvin, TX, Nov. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. R. H. Rosenwald, "Alkylation," pp. 890, 891 in Encylcopedia of Chemical Technology, 2d ed., vol. 1, edited by A. Standen et al., Interscience, New York, 1963.

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6. C. A. Peterson, IT Enviroscience, Trip Report for Visit to Union Carbide Corp., Institute, WV, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

7. Letter dated Feb. 17, 1978, from D. J. Lorine, Conoco Chemicals, Continental Oil Company, Inc., to D. R. Goodwin, EPA, Research Triangle Park, NC.

8. Letter dated Feb. 6, 1978, from E. A. Vistica, Witco Chemical, to D. R. Goodwin, EPA, Research Triangle Park, NC.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

The process emissions calculated for the LAB olefin process model plant* are based on information received from Monsanto, the only operator of the LAB olefin process in the United States. The process emissions calculated for the LAB chlorination process model plant are based on information received from Union Carbide, Conoco, and Witco, the three companies that operate chlorination process plants in the United States, and on data received from MCA, the State of Maryland Environmental Health Administration, and on data from EPA from a testing program. The emission quantities reported vary widely from plant to plant.[1--9]

A. LAB OLEFIN PROCESS[1,2]

1. Model Plant*

The model plant for the LAB olefin process has a capacity of 90 Gg/yr based on 8760 hr of operation per year.** Though this is not an actual operating plant, it is similar to the one existing plant in the United States. The model LAB olefin process, shown in Fig. III-1, reasonably conforms with current technology. A single process train is typical for today's manufacturing and engineering technology. The model process dehydrogenates n-paraffins to n-olefins and then reacts the n-olefins with benzene, with hydrogen fluoride used as the catalyst, to produce LAB.

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*See p. I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Typical raw material, intermediate, by-product, and product storage-tank capacities are estimated for a 90-Gg/yr plant. The storage-tank requirements are given in Table IV-1.

2. Sources and Emissions

All estimated process emission rates and sources for the LAB olefin process are summarized in Table IV-2.

a. Benzene Azeotrope Column Vent -- This column vent releases some benzene into the atmosphere. All benzene used in the process passes through the azeotrope column for removal of traces of water from the benzene. Since benzene freezes at 5.5°C (42°F), the column condenser must be operated above this temperature. At normal condenser temperatures of about 27°C (80°F), benzene has a vapor pressure of 13.7 kPa, and some benzene is normally lost out of the column vents.

b. Hydrogen Fluoride Scrubber Vent -- The largest process vent is the hydrogen fluoride scrubber vent. This scrubber receives vent gas from the alkylator and the benzene stripping column. In the uncontrolled model plant these process vent streams contain significant quantities of benzene and other VOC, as well as hydrogen fluoride vapor and system nitrogen purge gas. The hydrogen fluoride scrubber removes hydrogen fluoride from the vent stream by reacting it with alkaline (calcium hydroxide) scrubber water. Benzene and other VOC condense in this scrubber water. The scrubber normally operates at 32 to 38°C. The nitrogen is purged through the alkylation system at a flow rate of about 1.7 m^3/hr to prevent the backflow of water vapor into any of the system components. This flow of purge gas sweeps volatile benzene vapor out of the scrubber vent at an estimated rate of about 0.11 kg/hr. This is the largest process loss of benzene to the atmosphere. The increased use of nitrogen purge gas during startups or shutdowns, as well as process upsets, can drastically increase this normal loss rate by a factor of 5 to 10.

c. Vacuum Refining Column Vents -- The three product refining columns that operate under vacuum discharge the exhaust gases from their vacuum pump (steam jets) vents directly to the atmosphere. Since these columns operate at high head temperatures, the main column condensers must operate hot to prevent cooling of the reflux that is returned to the top of the columns. Auxiliary vent condensers

Table IV-1. LAB Olefin Model-Plant Storage (Organics Only)

Contents	Tank Size (m^3)	Turnovers Per Year	Molecular Weight	Bulk Liquid Temperature (°C)
n-Paraffin (11)[a] (bulk)	3200	10	164	32
n-Paraffin (12)[a] (bulk)	3200	10	175	32
n-Paraffin (13)[a] (bulk)	3200	10	186	32
n-Paraffin (feed)	213	230	175	32
n-Paraffin (feed)	213	230	175	32
n-Olefin (feed)	213	230	173	32
n-Olefin (feed)	213	230	173	32
Benzene (bulk)	3200	13	78	27
Benzene (feed)	213	200	78	27
Benzene (dry feed)	213	200	78	27
By-product (receiver)	18	150	118	38
By-product (bulk)	213	13	118	38
Heavies (receiver)	18	255	420	43
Heavies (bulk)	334	14	420	43
LAB (receiver)	213	250	243	43
LAB (receiver)	213	250	243	43
LAB (11)[a] (bulk)	334	15	236	43
LAB (12)[a] (bulk)	334	15	243	43
LAB (13)[a] (bulk)	334	15	261	43
LAB (11)[a] (bulk)	3200	11	236	43
LAB (12)[a] (bulk)	3200	11	243	43
LAB (13)[a] (bulk)	3200	11	261	43

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[a] Average chain length.

Table IV-2. Benzene and Total VOC Uncontrolled Emissions for 90-Gg/yr Model Plant Using the LAB Olefin Process

Source	Stream Designation (Fig. III-1)	Emission Ratio (g/Mg)[a]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Benzene azeotrope column vent	A_1	3.7	3.7	0.038	0.038
Hydrogen fluoride scrubber column vent	A_2	11	11	0.11	0.11
Paraffin stripping column vent	A_3		88		0.9
By-product stripping column vent	A_4		1		0.01
LAB product column vent	A_5		0.0014		0.000014

[a] g of emission per Mg of LAB produced.

have been provided on these column vacuum lines to prevent flooding of the vacuum pumps with hot vapors. Column air leakage and vapor pressure in the vent condenser determine the amount of VOC in the vacuum pump vents. Process upsets, startups, and shutdowns do not have much impact on the VOC emissions from these vents.

d. Other Emissions -- Storage, fugitive, and secondary emissions for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.[10--12]

B. LAB CHLORINATION PROCESS[3--9]

1. Model Plant

The model plant for this study has a capacity of 90 Gg/yr based on 8760 hr of operation per year. Although the model plant is not in actual operation, it is similar in most design features to the three existing plants in the United States. The model plant is sized midway between the two largest LAB chlorination process domestic plants. The model LAB chlorination process, shown in Fig. III-2, is a reasonable concept of current technology. A single process train is typical for today's manufacturing and engineering technology. The model process chlorinates *n*-paraffins to monochlorinated *n*-paraffins and then reacts the crude chloroparaffin with benzene in the presence of aluminum chloride catalyst to form the crude, linear alkylbenzene (LAB) products. Product separation, distillation, and final purification steps are used for separating and refining the final LAB products and for removal of the by-products and recycle materials.

Typical raw material, intermediate, by-product, and product storage-tank capacities are estimated for a 90-Gg/yr plant. The storage-tank requirements are given in Table IV-3.

2. Sources and Emissions

Estimated process emission rates and sources for the LAB chlorination process are summarized in Table IV-4.

Table IV-3. LAB Chlorination Model-Plant Storage (Organic Only)

Contents	Tank Size (m^3)	Turnovers Per Year	Molecular Weight	Bulk Liquid Temperature (°C)
n-Paraffin (11)[a] (bulk)	3200	10	164	32
n-Paraffin (12)[a] (bulk)	3200	10	175	32
n-Paraffin (13)[a] (bulk)	3200	10	186	32
n-Paraffin (feed)	213	230	175	32
n-Paraffin (feed)	213	230	175	32
n-Paraffin (dry feed)	640	225	175	32
n-Paraffin (dry feed)	640	225	175	32
Crude chloroparaffin (feed)	640	225	210	32
Crude chloroparaffin (feed)	640	225	210	32
Benzene (bulk)	3200	13	78	27
Benzene (feed)	870	240	78	27
Benzene (dry feed)	870	240	78	27
Waste oil (receiver)	18	150	118	32
Waste oil (bulk)	213	12	118	32
By-product (receiver)	40	200	118	38
By-product (bulk)	640	12	118	38
Heavies (receiver)	80	260	420	43
Heavies (bulk)	1420	15	420	43
LAB (receiver)	213	250	243	43
LAB (receiver)	213	250	243	43
LAB (11)[a] (bulk)	334	15	236	43
LAB (12)[a] (bulk)	334	15	243	43
LAB (13)[a] (bulk)	334	15	261	43
LAB (11)[a] (bulk)	3200	11	236	43
LAB (12)[a] (bulk)	3200	11	243	43
LAB (13)[a] (bulk)	3200	11	261	43

[a] Average chain length.

Table IV-4. Benzene and Total VOC Uncontrolled Emissions from LAB Chlorination Process Used in 90-Gg/yr Model Plant

Source	Stream Designation (Fig.III-2)	Emission Ratio (g/Mg)[a]		Emission Rate (kg/hr)	
		Benzene	Total VOC	Benzene	Total VOC
Paraffin drying column vent	A_1		2.8		0.029
Benzene azeotrope column vent	A_2	3.7	3.7	0.038	0.038
Hydrochloric acid absorber vent	A_3	250	250	2.6	2.6
Atmospheric wash decanter vents	A_4	12.3	12.4	0.126	0.127
Benzene stripping column vent	A_5	3.7	3.7	0.038	0.038
Vacuum refining column vents[b]	A_6		92		0.95

[a] g of emissions per Mg of LAB produced.

[b] Assumed use of refrigerated vent condensers to minimize venting of VOC vapors through the vacuum pumps on the vacuum refining column vents.

a. *n-Paraffin Drying Column Vent* -- The *n*-paraffin drying column operates under vacuum to keep the still bottoms temperature below the *n*-paraffin decomposition range. The primary reflux condenser operates at high head temperature to prevent subcooled reflux from being returned to the top of the column. An auxiliary vent condenser is provided to prevent flooding of the vacuum pump with hot vapors. Column air leakage and vapor pressure in the vent condenser determine the amount of VOC in the vacuum pump vent. Normal leakage rates were assumed to permit calculation of estimated emissions. Process upsets, startups, and shutdowns do not have much impact on the VOC emissions from this vent.

b. *Benzene Azeotrope Column Vent* -- This column vent releases some benzene into the atmosphere. All benzene used in the process passes through the azeotrope column for removal of traces of water from the benzene. Since benzene freezes at 5.5°C (42°F), the column condenser must be operated above this temperature. At normal condenser temperatures of about 27°C (80°F) benzene has a vapor pressure of 13.7 kPa, and some benzene is normally lost out of the column vent.

c. *Hydrogen Chloride Absorber Vent* -- This vent is the largest process vent for the LAB chlorination process. All of the vent gas from the paraffin chlorinators and the alkylation reactors is directed first through a volatile organic absorber system and then through the acid absorber before being discharged to the atmosphere. The amount of VOC in the hydrogen chloride gas going to the acid absorber is regulated by the performance of the volatile organic absorber system. All the crude chloroparaffin is used as the absorption fluid in the volatile organic absorber. The principal VOC that escape from the organic absorption system is benzene, with some traces of *n*-paraffin and paraffin degradation products. The acid absorption system operates as an adiabatic absorber, with the heat of solution of the hydrogen chloride in water raising the temperature of the acid solution to the boiling point to prevent absorption of VOC in the acid. (Absorption of VOC in the acid by-product would contaminate the acid with dissolved organic material, and its removal would be necessary if the acid were sold.) The nitrogen purge gas charged to the alkylator escapes through the vent from the hydrogen chloride absorber, carrying with it the residual VOC that escapes from the volatile organic absorber system. (Nitrogen is purged through the alkylator at a flow rate of about 1.7 m^3/hr to prevent backflow of water vapor into any of the alkylator system components.) Variations in inert-gas content in the chlorine gas used for chlorination also influence this gas flow. The increased use of nitrogen purge gas during startups or shutdowns, as well as process upsets, can drastically increase this normal loss rate by a factor of 5 to 10. Benzene emissions from this vent as reported by industry vary from about 5 g/Mg of LAB to over 10,000 g/Mg (see Appendix B).

d. Atmospheric Wash and Decanter Vents -- The series of process vessels used for settling the catalyst slurry, hydrolyzing the spent catalyst, neutralizing the organic product stream, washing the organic product stream, and decanting the various oil layers from the various hydrolysis, neutralization, and wash water streams are all vented to the atmosphere through conservation vents. Since these vessels normally operate at constant liquid levels, the only VOC losses are breathing losses. Startups, shutdowns, and process upsets could drastically increase this loss by vapor space displacement due to changes in liquid levels.

e. Benzene Stripping Column Vent -- The benzene stripping column operates at atmospheric pressure, and the vent line from the condenser reflux receiver vents to the atmosphere. Since benzene has a significant vapor pressure (24.3 kPa) at the column condenser temperature of about 40°C, some benzene vapors are lost to the atmosphere at this point.

f. Vacuum Refining Column Vents -- The three product refining columns that operate under vacuum discharge the exhaust gases from their vacuum pump vents directly to the atmosphere. Since these columns operate at high head temperatures, the main column condensers must operate hot to prevent subcooled reflux from being returned to the top of the columns. Auxiliary vent condensers have been provided on these column vacuum lines to prevent flooding of the vacuum pumps with hot vapors. Column air leakage and vapor pressure in the vent condenser determine the amount of VOC in the vacuum pump vents. Process upsets, startups, and shutdowns do not have much impact on the VOC emissions from these vents.

g. Other Sources -- Storage, fugitive, and secondary emissions for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.[10--12]

C. REFERENCES*

1. C. A. Peterson, IT Enviroscience, Trip Report for Visit to Monsanto Industrial Chemicals Co., Alvin, TX, Nov. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC.).
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3. C. A. Peterson, IT Enviroscience, Trip Report for Visit to Union Carbide Corp., Institute, WV, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
4. Letter dated May 16, 1979, from R. L. Foster, Union Carbide Corp., South Charleston, WV, to D. R. Patrick, EPA, with comments on draft LAB report.
5. Letter dated Feb. 6, 1978, from E. A. Vistica, Vice President, Witco Chemical Corporation, Wilmington, CA, to D. R. Godwin, Director, ESED Division, EPA.
6. Letter dated Feb. 17, 1978, from D. J. Lorine, Chief Engineer, Conoco Chemicals Div., to D. R. Godwin, Director, ESED Division, EPA.
7. Letter dated Apr. 26, 1979, from R. A. Oliver, Public Health Engineer, State of Maryland Environmental Health Administration, Baltimore, MD, to D. R. Patrick ESED, EPA, with comments on draft LAB report.
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11. D. G. Erikson and V. Kalcevic, IT Enviroscience, Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).
12. J. Cudahy and R. Standifer, IT Enviroscience, Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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*Usually, when a reference located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. LAB OLEFIN PROCESS

1. Hydrogen Fluoride Scrubber Vent

The main process vent for the LAB olefin process is the vent from the hydrogen fluoride scrubber column. The vent gas from this column is rich in benzene vapor, releasing approximately 11 g of benzene per Mg of LAB product. An emission control system is the destruction of the hydrogen fluoride scrubber vent vapors by combustion.

Since a flare stack system would have to be installed for control of emergency emissions due to process upsets and malfunctions, this hydrogen fluoride scrubber vent emission stream could be directed to the flare stack for destruction by combustion. Properly designed flare tips with steam or air injection and continuous pilot lights can assure combustion of flammable vapors at removal efficiencies of 90%* or better.[1] This control method is used by industry to control the emissions from a hydrogen fluoride vent (see Appendix B).

Another possible control technique is to use the emissions from the hydrogen fluoride scrubber vent and the benzene azeotrope column vent as fuel by piping the vent gases into the plant fuel gas header where one is used. The VOC destruction efficiency for this technique can be greater than 99.98%.[1,2] This control method is used by industry on other processes, and the incremental cost for connecting the vent to the fuel gas header should be negligible when done as a new plant is being designed.

2. n-Paraffin Stripping Column Vent

This secondary process vent for the LAB olefin process is rich in n-paraffin vapor, releasing approximately 88 g of n-paraffin per Mg of LAB product. For a 90-Gg/yr plant the yearly emissions from this source would be approximately 7.9 Mg.

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*Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies cited are for tentative comparison purposes.

a. Reduction of Air In-Leakage -- The vent emissions calculated for this n-paraffin stripping column are based on the assumption of an air in-leakage rate typical of a normally assembled and maintained vacuum distillation column with no special precautions or techniques used to achieve better than average column tightness. Special testing, maintenance, and assembly techniques can be used to reduce this air in-leakage rate and the resultant VOC emissions.

b. Condensation of Jet Exhaust -- The uncontrolled model plant shows a single-stage steam jet as the vacuum pump on the n-paraffin stripping column, with the steam and entrained vapors discharging directly to the atmosphere. Addition of a surface condenser to condense and subcool the steam and entrained vapors to about 38°C would remove at least 92% of the n-paraffin vapors from this vent stream.[3] The condensate would contain the condensed n-paraffin, and this condensate stream could be sent to the plant wastewater skimmer system for separation and recovery of the n-paraffin organic layer. The controlled emissions from this surface condenser are shown in Table V-1.

3. Other Process Vents

The emissions from the other process vents (lights stripping column and LAB product column) are already low enough to warrant no further effort to reduce VOC from these process vents.

4. Fugitive Sources

Controls for fugitive sources are discussed in another EPA report covering fugitive emissions from the synthetic organic chemicals manufacturing industry.[4]

5. Storage and Handling Sources

Control of benzene and other VOC storage emissions for the synthetic organic chemicals industry is covered in another EPA report.[5]

6. Secondary Sources

Controls for secondary emissions from the synthetic organic chemicals industry are discussed in another EPA report.[6]

Table V-1. Benzene and Total VOC Controlled Emission for 90-Gg/yr Model Plant Using the LAB Olefin Process

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	Emissions			
				Ratio (g/Mg)[a]		Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Benzene azeotrope column vent	A_1	Used as fuel	99.98	0.00074	0.00074	0.0000076	0.0000076
Hydrogen fluoride scrubber column vent	A_2	Used as fuel (Alt 1)	99.98	0.0022	0.0022	0.000023	0.000023
		Flare (Alt 2)	90	1.1	1.1	0.011	0.011
Paraffin stripping column vent	A_3	Surface condenser	92		7.0		0.072
Lights stripping column vent	A_4	None[b]			1.0		0.01
LAB product column vent	A_5	None[b]			0.0014		0.000014

[a] g of benzene or total VOC per Mg of LAB produced.

[b] Jet exhaust surface condenser recommended for suppression of steam plume.

B. LAB CHLORINATION PROCESS

1. Hydrochloric Acid Absorber Vent

The main process vent for the LAB chlorination process is the vent from the hydrochloric acid absorber. The vent gas from this absorber column is rich in benzene vapor, releasing approximately 250 g of benzene per Mg of LAB product. The only control technique reported for this vent is the operation of the hydrochloric acid absorber so that benzene goes with the aqueous acid, followed by removal of the benzene from the acid by an oil-water separator and activated carbon. No data were given on the removal efficiency achieved when this technique is used. Emission of benzene at one plant was reported as 50 g per Mg of LAB produced (see Appendix B).

Another control technique for this vent is to scrub the vent gases with caustic and pipe the neutralized vent gases into a plant fuel-gas header if one is used. The VOC destruction efficiency for this control technique can be greater than 99.98%.[1,2] This method is used to control alkylation vent gases from the manufacture of ethylbenzene. An alternative is to pipe the neutralized vent gases to a flare, a technique that is used by industry for other processes.[7] The incremental cost for using either of these techniques in a new plant is negligible.

Another possible control technique is the use of carbon adsorption. In order to use carbon adsorption, the exhaust gas stream must be scrubbed with caustic to remove acid and water-soluble organics. Benzene is likely the only VOC remaining. Two or more carbon beds are needed since the exhaust stream passes through one bed while the other bed is being regenerated with steam. The steam condensate is decanted to separate the benzene for recycle to the process, and the benzene-saturated aqueous layer is sent to waste disposal. This control technique has not been demonstrated on this vent stream, but based on engineering experience with similar applications it is believed that a carbon adsorption system can be designed and operated at a sustained removal efficiency of greater than 99%.[8]

A removal efficiency of 99.98% for use of the vent gases as fuel has been used to project the controlled hydrochloric acid absorber vent emissions from the model plant (Table V-2).

Table V-2. Benzene and Total VOC Controlled Emissions for 90-Gg/yr Model Plant Using LAB Chlorination Process

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	Emissions			
				Ratio (g/Mg)[a]		Rate (kg/hr)	
				Benzene	Total VOC	Benzene	Total VOC
Paraffin azeotrope column vent	A_1	Used as fuel	99.98		0.00056		0.0000058
Benzene azeotrope column vent	A_2	Used as fuel	99.98	0.00074	0.00074	0.0000076	0.0000076
Hydrochloric acid absorber vent	A_3	Used as fuel	99.98	0.05	0.05	0.00051	0.00051
Atmospheric wash decanter vents	A_4	Used as fuel	99.98	0.0025	0.0025	0.000025	0.000025
Benzene stripping column vent	A_5	Used as fuel	99.98	0.00074	0.00074	0.0000076	0.0000076
Vacuum refining column vents	A_6	Used as fuel	99.98		0.018		0.00019

[a] g of benzene or total VOC per Mg of LAB produced.

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2. n-Paraffin Azeotrope Column Vent

A vacuum vent condenser is incorporated in the design for the n-paraffin azeotrope column vent to prevent flooding of the vacuum pump with hot n-paraffin vapors. The VOC remaining that are emitted from the vacuum pump discharge of the model plant are controlled by being piped to the plant fuel-gas header for use as fuel. A VOC destruction efficiency of 99.98%[1,2] was used to calculate the controlled emissions that originate in this vent, as was done for all process vents in the model plant (see Table V-2). An alternative control technique could consist in piping the emissions to the emergency flare or to the carbon adsorber if one of those techniques is used for controlling the hydrochloric acid absorber vent.

3. Benzene Azeotrope Column Vent

The emission control selected for this vent for the model plant is the use of the vent gases as fuel and a VOC destruction efficiency of 99.98%[1,2] was used to calculate the model-plant controlled emissions from this vent.

4. Atmospheric Wash-Decanter Vents

These series of wash-decant process vessels are tied together by one common vent line, padded with nitrogen, and terminated with a conservation vent. The emissions from this vent are breathing losses that are controlled in the model plant by using them as fuel. A VOC destruction efficiency of 99.98%[1,2] was used to calculate the model plant controlled emissions from this vent.

5. Benzene Stripping Column Vent

The emission control selected for this vent for the model plant is the use of the vent gases as fuel. A VOC destruction efficiency of 99.98%[1,2] was used to calculate the model-plant controlled emissions from this vent.

6. Vacuum Column Vents

The n-paraffin stripping column vent is rich in n-paraffin vapor, releasing approximately 88 g of n-paraffin per Mg of LAB product for a 90 Gg/yr plant. The emissions from the n-paraffin stripping column vent and from the other vacuum columns are controlled in the model plant by using them as fuel. A VOC destruction efficiency of 99.98%[1,2] was used to calculate the model-plant controlled emissions from this vent.

7. Fugitive Sources

Controls for fugitive sources are discussed in another EPA report covering fugitive emissions from the entire synthetic organic chemicals manufacturing industry.[4]

8. Storage and Handling Sources

Control of benzene and other VOC storage emissions for the entire synthetic organic chemicals industry is covered in a separate EPA report.[5] Information on LAB manufacturing locations indicates that benzene is stored in both fixed-roof and floating-roof API style tanks. A floating roof is commonly used to control storage-tank emissions for VOC in the vapor pressure range of benzene. The vapor pressures of all the other organic raw materials, intermediates, and finished products or by-products are low. The vent lines on these storage tanks could be interconnected and the final output vent sent to some control device or system if it were cost effective.

9. Secondary Sources

Control of secondary emissions is discussed in a separate EPA report.[6]

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C. REFERENCES*

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2. T. Lahre, "Natural Gas Combustion," pp. 1.41—1.4-3 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (May 1974).

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VI. IMPACT ANALYSIS

A. ENVIRONMENTAL IMPACT

Tables VI-1 and VI-2 show the environmental impact of reducing VOC emissions by application of the described control devices or techniques (Sect. V) to new plants producing 90 Gg/yr of LAB by the model olefin process and by the model chlorination process respectively. The environmental impacts of controlling VOC emissions from storage and handling, fugitive, and secondary sources are not included in the estimates in Tables VI-1 and VI-2 but are believed to be similar to those from other processes in the synthetic organic chemicals manufacturing industry.

Based on a projected estimate of 290 Gg of LAB produced in 1980 and on a current removal efficiency of approximately 10%, a very rough estimate of emissions from the LAB industry in 1980 is 1200 Mg of benzene and 1400 Mg of total VOC. This estimate includes process, storage and handling, fugitive, and secondary sources. If planned retrofitting of emission controls has been completed, the estimate may be high (see Appendix B), depending on the reduction efficiency actually achieved.

B. OTHER IMPACTS

Energy and control cost impacts have not been determined for the control techniques selected in Sect. V. The impacts are believed to be negligible when the techniques are applied during the design of a new plant.

Table VI-1. Environmental Impact of Controlled LAB Olefin 90-Gg/yr Model Plant

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				Benzene	Total VOC
Benzene azeotrope column vent	A_1	Used as fuel	99.98	0.33	0.33
HF scrubber column vent	A_2	Used as fuel	99.98	0.99	0.99
		Flare	90	0.89	0.89
Paraffin stripping column vent	A_3	Surface condenser	92		7.3
Lights stripping column vent	A_4	None			
LAB product column vent	A_5	None			

Table VI-2. Environmental Impact of Controlled LAB Chlorination 90-Gg/yr Model Plant

Source	Stream Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				Benzene	Total VOC
Paraffin azeotrope column vent	A_1	Used as fuel	99.98		0.25
Benzene azeotrope column vent	A_2	Used as fuel	99.98	0.33	0.33
Hydrochloric acid absorber vent	A_3	Used as fuel	99.98	22.5	22.5
Atmospheric wash decanter vents	A_4	Used as fuel	99.98	1.1	1.1
Benzene stripping column vent	A_5	Used as fuel	99.98	0.33	0.33
Vacuum refining column vents	A_6	Used as fuel	99.98		8.3

APPENDIX A

Table A-1. Physical Properties of Benzene[a]

Synonyms	Benzol, coal naphtha, phenylhydride
Molecular formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Vapor pressure	95.9 mm Hg at 25°C
Vapor specific gravity	2.77
Boiling point	80.1°C at 760 mm Hg
Melting point	5.5°C
Liquid specific gravity	0.8787 at 20°C/4°C
Water solubility	1.79 g/liter
Octanol/water partition coefficient	2.28

[a] From: J. Dorigan et al., "Benzene," p. AI-102 in Scoring of Organic Air Pollutants, Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

Table A-2. Typical Physical Properties of *n*-Paraffins*

	Low-Range Value	Mid-Range Value	High-Range Value
Chain distribution (%)			
Below C_{10}	<2		
C_{10}	16	<2	
C_{11}	38	1	<1
C_{12}	40	16	20
C_{13}	6	51	47
C_{14}	1	32	23
C_{15}		1	8
C_{16}			2
Average molecular weight	161	189	186
Specific gravity at 60°F	0.745	0.756	0.767
Flash point (°F) (Pensky-Martin)	155	210	210
Melting range (°C)	-22 to -25	-11 to -13	-3 to 0
Viscosity at 60°F (cs)	1.78	2.80	
Distillation range (°F)			
Initial boiling point	360	435	435
50%	386	453	
90%	408	468	
End point	446	482	558

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*Abstracted from *Conoco Normal Paraffins*, Conoco Chemicals Division, Continental Oil Co., Houston, TX (nd).

Table A-3. Typical Physical Properties of Linear Alkylbenzenes*

	Low-Range Value	Mid-Range Value	High-Range Value
Chain distribution (%)			
Below C_{10}	<2	<0.5	
C_{10}	18	10	<0.5
C_{11}	32	28	1.5
C_{12}	37	39	15
C_{13}	10	15	47
C_{14}	>2	7	34
C_{15}		<0.5	<3
C_{16}			
Average molecular weight	238	244	262
2-Phenyl isomer (%)	20—40	20—30	20—30
Specific gravity at 60°F	0.866	0.865	0.865
Viscosity at 100°F (cs)	4.3	4.7	5.9
Bromine number	0.003	0.01	0.01
Flash point (°F) (Pensky-Martin)	280-290	290-300	295-305
Distillation range (°F)			
Initial boiling point	536	543	577
5%	546	553	588
50%	555	563	597
95%	578	593	615
End point	586	603	621

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[*] Abstracted from: Conoco Nalkylene 500 Detergent Alkylate, Conoco Chemicals Division, Continental Oil Co., Houston, TX (nd), Product Data Sheet (on Alkylate A215, A225, & A230), Monsanto Industrial Chemicals Co., St. Louis, MO (December 1976); Product Information. UCANE Alkylate 12 Linear 11 and 12 Alkylbenzene, Union Carbide Corp., New York (nd).

Table A-4. Typical Physical Properties of LAB By-Products*

	LMR*	DPA*	NDB*
Average molecular weight	400	310	
Specific gravity at 60°F	0.883	0.888	0.891
Flash point (°F) (Pensky-Martin)	415—430	380	380
Pour point (°F)		-70	-60
Viscosity			
at 60°F	125		
at 100°F		14	
at 122°F			14
Distillation range (°F)			
Initial boiling point		626	680
5%		642	730
50%		682	800
95%		714	975

* Abstracted from: Conoco LMR (Low Molecular Ratio), Conoco N-B-D (Distilled Total Nathylene 500 Bottoms) and Conoco DPA (Diphenylalkane), product bulletins, Conoco Chemicals Division, Continental Oil Co., Houston, TX (nd).

APPENDIX B

EXISTING PLANT CONSIDERATIONS

Tables B-1[1] and B-2[2--4] list the emission control devices and techniques reported to be in use by the LAB industry. To gather information for this report, two site visits were made to manufacturers of LAB. Trip reports have been cleared by the companies concerned and are on file at ESED in Durham, NC.[1,2] Some of the pertinent information concerning process emissions from these existing LAB plants is presented in this appendix. Other information is from letters to EPA from the other two companies that produce LAB, in response to requests for information on process emissions from their plants.[3,4] Also included is information received with comments on the draft Linear Alkylbenzene Report.[5--7]

A. CONTROLS AT EXISTING PLANTS

1. Monsanto, Alvin, TX[1,5]

Monsanto is the only operator of the LAB olefin process in the United States and uses a process developed by Monsanto using refining and reaction principles originally developed in the petroleum refining industry. See Table B-1 for the emission control devices and techniques used by Monsanto. No measurements of emissions were reported; however, Monsanto believes its process should not require additional controls. See Table B-3 for Monsanto's estimates of actual emission ratios for its process.

2. Union Carbide, Institute, WV[2,6]

The Union Carbide plant uses the paraffin chlorination process for production of LAB. See Table B-2 for the emission control devices and techniques used by Union Carbide. Table B-4 gives the emissions reported by Union Carbide. In the Union Carbide plant the HCl gas stream from the alkylation reaction is scrubbed with all the crude chlorinated paraffin to remove benzene and then is sent to limestone "pits," where the HCl is neutralized. Union Carbide and EPA have sampled this gas stream and analyzed it for organic content. The reported presence of relatively large quantities of compounds that cannot be reasonably accounted for and the inability to calculate a material balance from the data are reasons for doubting the results of the EPA study. Union Carbide reports that VOC losses with the wastewater from their LAB process are from 3 to 5 kg of VOC per Mg of LAB produced. This wastewater goes to their plant wastewater system. Their

Table B-1. Control Devices and Techniques Currently Used in the LAB Olefin Process

Source	Stream Designation (Fig. III-1)	Emission Control Devices and Techniques*
Benzene azeotrope control vent	A_1	None
Hydrogen fluoride scrubber column vent	A_2	Vent gases sent to flare for combustion
Paraffin stripping column vent	A_3	Vent condenser used to minimize VOC to vacuum jet; no condenser used on jet exhaust
Lights stripping column vent	A_4	Vent condenser used to minimize VOC to vacuum jet
LAB product column vent	A_5	Vent condenser used to minimize VOC to vacuum jets; surface condenser used as intercondenser between second-stage jet and final steam jet
Storage and handling emissions	C	Refrigerated vent condenser used to reduce emissions from fixed-roof benzene storage tank used to feed process
Fugitive emissions	J	Mechanical single and double seals used on centrifugal pumps; quality of maintenance on valves, etc., not known, but plant appeared to be clean and neat; special precautions used during plant shutdowns and turnarounds
Secondary emissions	K	Plant wastewater streams combined, put through an enclosed skimming tank to remove floating organics; then skimmed, filtered wastewater fed to a deep-well injection system for disposal; filtered solids are then sent to land fill; organic skimmings are recovered and returned to the process or are burned as fuel

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* Used by Monsanto; see ref 1.

Table B-2. Control Devices and Techniques Currently Used in the LAB Chlorination Process

Source	Stream Designation (Fig. III-2)	Control Devices and Technologies Used		
		By Union Carbide[a]	By Conoco[b]	By Whitco[c]
Paraffin drying column vent	A_1	None	None	Sent to heater for oxidation
Benzene azeotrope column vent	A_2	None	None	Sent to heater for oxidation
Hydrochloric acid absorber vent	A_3	None	None	Removed by oil/water separator and activated carbon adsorption
Atmospheric wash decanter vents	A_4	None	None	Sent to heater for oxidation
Benzene stripping column vent	A_5	None	None	Sent to heater for oxidation
Vacuum refining column vents	A_6	None	None	Surface condensers used to condense jet exhaust; residual exhaust sent to heater for oxidation
Storage and handling emissions	C	Insulation of benzene storage tanks	Not reported	Not reported
Fugitive emissions	J	Single and double mechanical seals used on pumps handling VOC	Not reported	Not reported
Secondary emissions	K	Skimmer used to remove floating VOC; wastewater sent to plant wastewater system	Not reported	Wastewater scrubbed with air to remove benzene and other VOC; air from scrubber sent to heater for oxidation

[a] See ref 2.

[b] See ref 3.

[c] See ref 4.

Table B-3. Estimated Emissions from Monsanto LAB Plant[a]

	Emission Ratio (g/Mg)[b]			
	Potential		Actual Existing	
Source	Benzene	VOC	Benzene	VOC
Benzene drying vent	3.7	3.7	3.7	3.7
HF scrubber vent	11.0	11.0	1.1	1.1
Paraffin stripper vent		88.0		88
Lights stripper vent		1		1
LAB prod. column vent		0.0014		0.0014
Storage and handling	602	668	141.1	203.1
Fugitive emissions	4.9	20.3	4.9	20.3
Secondary emissions	71	142.0	16	33
Total emissions	692.6	933	166.8	350.2

[a] See ref 5.

[b] g of emission per Mg of LAB produced.

Table B-4. Emissions from Union Carbide LAB Plant[a]

Source	Emission Ratio (g/Mg)[b]
Catalyst tank vent	72
Water scrubber on sludge destruction decanter vent	2
Wash-decantation vent	0.026
Stills	3
Benzene storage	3.3

[a] See refs 2 and 6.

[b] g of emissions per Mg of LAB produced.

plant differs from the model plant by having a vent on the catalyst mix tank. This vent is needed to discharge the nitrogen that is used to force the catalyst from the storage bins into the tank containing benzene. The tank is agitated and operates at atmospheric pressure.

3. Conoco, Baltimore, MD[3,7]

The Conoco plant was at one time estimated to be emitting more than 3 tons of benzene per day. It employs the paraffin chlorination process but differs from the model plant in that (1) Conoco uses a molecular sieve for drying the feed benzene, (2) the HCl absorbers are not operated to minimize absorption of benzene, (3) the $AlCl_3$ catalyst sludge recovery is vented separately, and (4) the sprung oil settler is vented separately. The estimated emissions from the Conoco LAB plant are given in Table B-5. Conoco reported plans for retrofit emission control to several of these sources by late 1978. In ref. 7 it is reported that the need for a vent on the $AlCl_3$ catalyst sludge recovery system was eliminated by installation of a static mixer, which cut the emission from that vent to zero. Conoco also reported that a paraffin absorber was proposed as a control on several of the vents shown in Table B-5 and an estimate of 5 ppm of benzene in the exit stream from the absorber. A spray tower was reported as the proposed control on the hydrochloric acid absorber vent and a surface aftercondenser was reported as the proposed control on the vacuum refining column vents, with a projection that the benzene in the vent gases from these control devices is minimal.

4. Witco Chemical, Carson, CA[4]

Witco reports that almost all of their benzene-containing vent gas streams are burned in their heater. The HCl absorber is operated so that the organics go with the muriatic acid; 18 lb of benzene and 36 lb of n-paraffin are removed from the muriatic acid by an oil-water separator and activated carbon. Approximately 40 gpm of wastewater containing 400 to 600 mg/liter of benzene is scrubbed with 250 to 300 scfh of air, which is then sent to the heater for oxidation of the benzene.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs

Table B-5. Estimated Emissions from Conoco LAB Plant[a]

Source	Benzene Emission Ratio (g/Mg)[b]
Hydrochloric acid absorber vent	62.5 (841)[c]
Atmospheric wash decanter vents	175 (7428)[c]
Benzene stripping column vent	526
Vacuum refining column vent	1073
$AlCl_3$ catalyst sludge recovery vent	3949
Sprung oil settling vent	131 (3898)[c]
Storage and handling	1472[d]
Fugitive emissions	No information
Secondary emissions	624[d]
Total	8012.5

[a] See refs 3 and 7.

[b] g of benzene per Mg of LAB produced.

[c] Numbers in paretheses are emission ratios calculated for flow at upset conditions by assuming that the concentration of benzene in the vent gases does not change. See ref 3.

[d] Emission ratios from ref 7, which states "the figures ... have been adjusted to a production rate similar to that of the model plant." No explanation is given for why ratios are expected to change with production rate. All other ratios were calculated from data in Conoco letter (ref 3).

associated with this difficulty, it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant. Connecting existing vents to existing flares or fuel header systems can require a significant smount of piping. Pressure considerations are more of a problem with existing equipment, which may not operate properly if back-pressure is increased with the addition of emission control equipment.

APPENDIX B REFERENCES*

1. C. A. Peterson, IT Enviroscience, Trip Report for Visit to Monsanto Chemicals Co., Alvin, TX, Nov. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. C. A. Peterson, IT Enviroscience, Trip Report for Visit to Union Carbide Corp., Institute, WV, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. Letter from D. J. Lorine, Chief Engineer, Conoco Chemical Division, to D. R. Godwin, Director, ESED Division, EPA, Feb. 17, 1978.

4. Letter from E. A. Vistica, Vice President, Witco Chemical Corp., Wilmington, CA, to D. R. Godwin, Director, ESED Division, EPA, Feb. 6, 1978.

5. Letter from J. H. Craddock, Manager, Product Safety, Monsanto Industrial Chemicals Co., St. Louis, MO, to D. R. Patrick, EPA, May 31, 1979, with comments on draft LAB report.

6. Letter from R. L. Foster, Union Carbide Corp., South Charleston, WV, to D. R. Patrick, ESED, EPA, May 16, 1979, with comments on draft LAB report.

7. Letter from R. A. Oliver, Public Health Engineer, State of Maryland Environmental Health Administration, Baltimore, MD, to D. R. Patrick, ESED, EPA, Apr. 26, 1979, with comments on draft LAB report.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX C

LIST OF EPA INFORMATION SOURCES

Letter from E. A. Vistica, Witco Chemical Corp., Wilmington, CA, to D. R. Godwin, EPA, ESED Division, Feb. 6, 1978.

Letter from D. J. Lorine, Conoco Chemicals Division, to D. R. Godwin, EPA, ESED Division, Feb. 17, 1978.

Harry M. Walker, Texas Air Control Board 1975 Emission Inventory Questionnaire for Monsanto Chemical Co., Chocolate Bayou, LA, Plant.